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ANTI-SEQUINORBORNENE

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An improved synthesis of *anti*-sesquinorbornene

by

Alan Joseph Miller

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

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An improved synthesis of *anti*-sesquinorbornene

submitted by: Alan Joseph Miller

in partial fulfilment of the requirements for the degree of Master of Science.

Karl R. Kopecky
Supervisor

R S Brown

Date 21 February 1983

ABSTRACT

A new synthetic method for the preparation of the olefin *anti*-sesquinorbornene from the anhydride 1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a,8a-dicarboxylic anhydride was developed. This method replaced the procedure of Bartlett (*J. Am. Chem. Soc.* **102**, 1383(1980)) by a series of chemical steps that gave the olefin in 21% overall yield. These chemical steps could be scaled-up much more easily than Bartlett's procedure which gave the olefin in about 20% yield by electrolytic bisdecarboxylation of the corresponding dicarboxylic acid. The acid-methyl ester made from the anhydride was treated with lead tetraacetate in refluxing benzene-acetic acid to form the acetoxy-methyl ester (65%). This was treated with refluxing 4.5 M sulfuric acid until the organic phase resolidified, usually 10-12 h, to form the β-hydroxy acid (95%). This was treated with benzenesulfonyl chloride in pyridine containing triethylamine at 95°C for 6 h under argon to form the olefin (34%). Failure to add triethylamine or treatment of the olefin with pyridinium hydrochloride in pyridine gave the chlorocarbon 4a-chloro-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene. This is the first reported example of the addition of hydrogen chloride to a double bond by pyridinium hydrochloride and might be due to the relief of angle strain around the carbon atoms of the double bond upon rehybridization from sp^2 to sp^3.

Bartlett found that the anhydride 1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,exo*-dimethanonaphthalene-4a,8a-dicarboxylic anhydride could not be hydrolyzed to the diacid by hot sulfuric acid or esterified by treatment with several bases. Treatment of this anhydride with sodium methoxide in absolute methanol at 150°C for 2 days gave the corresponding dicarboxylic acid (82%). Shorter reaction times gave the acid-methyl ester. Initial formation of the carboxylate-methyl ester followed by an S_N2 reaction of methoxide ion with the methyl group of the ester is responsible for the formation of the diacid under these anhydrous conditions.

3,4:3,4-*exo,endo*-Di(1,3-cyclopentano)-1,2-dioxetane decomposed to give light immediately at all temperatures required for its formation from either the *B*-bromo-or iodohydroperoxide precursors by treatment with silver acetate in dichloromethane and could not be isolated. Surprisingly, light was also emitted when TLC plates (silica gel) or benzene solutions containing just these precursors were heated. This has not been reported for other *B*-halohydroperoxides.

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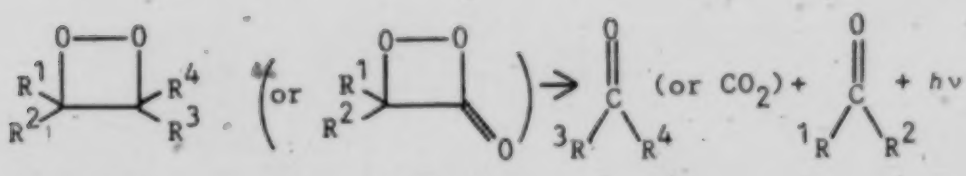
INTRODUCTION

Long before they were actually prepared and isolated, 1,2-dioxetanes (D) and the related α-peroxylactones (L) had been proposed as key intermediates in numerous chemi- and bioluminescent reactions (eq 1)[1]. At that time few thought that such unstable looking intermediates would

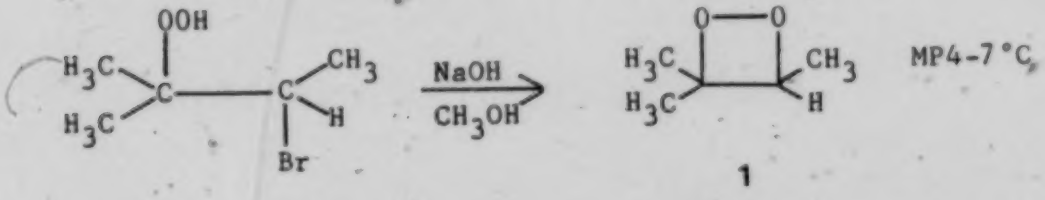
(1)



D L

ever be isolated. The release of ring strain and the formation of two strong carbonyl bonds at the expense of only one C-C bond and a weak O-O bond should greatly favor their decomposition. Thus, there was much surprise when Kopecky and Mumford[2] reported the synthesis (eq 2) of dioxetane **1**,

(2)

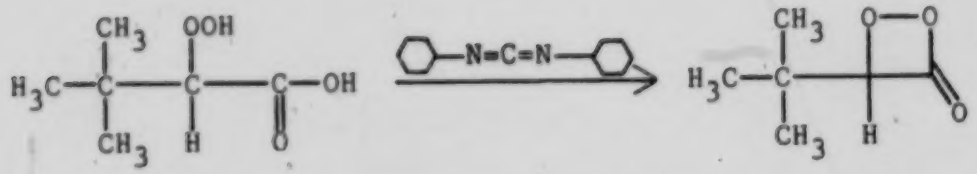


1

a relatively stable molecule that upon heating decomposed according to eq 1 to yield acetone, acetaldehyde and a bluish light. Since this report, many papers have appeared involving the synthesis and properties of 1,2-dioxetanes and α-peroxylactones, and have been recently

reviewed[3,4,5]. The first α-peroxylactone, 2, was synthesized (eq 3) by Adam[6] and shown to emit light as in eq 1.

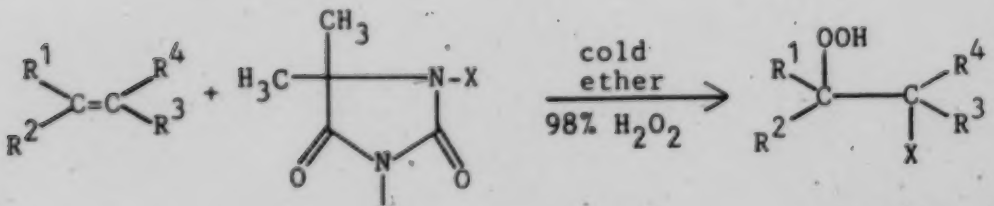
(3)



2

Three methods have been developed for preparing 1,2-dioxetanes, all starting from the corresponding olefin. The first involves initial treatment of the olefin with 1,3-dihalo-5,5-dimethylhydantoin (3) and excess 98% hydrogen peroxide in cold ether to yield the β-halohydroperoxide (eq 4)[7,8]. This reaction proceeds by an ionic mechanism.

(4)

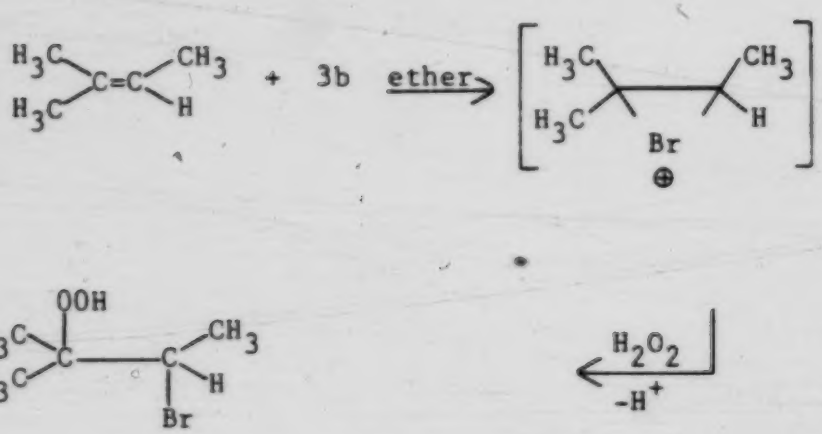


3a, X=Cl
3b, X=Br
3c, X=I

For unsymmetrical olefins (eq 5)[7], hydrogen peroxide reacts with the carbon atom best able to accommodate positive

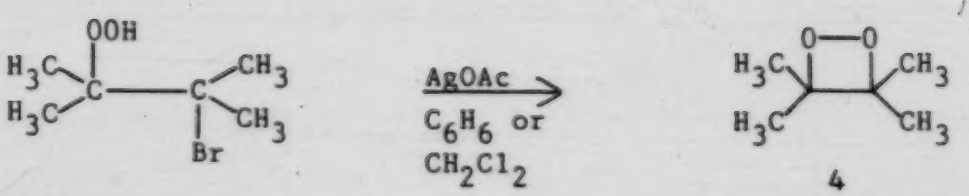
charge. The β-halohydroperoxide is then treated with basic

(5)



methanol (eq 2) or with a silver salt in a suitable solvent (eq 6)[8a].

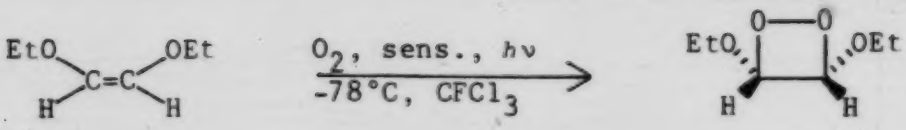
(6)



4

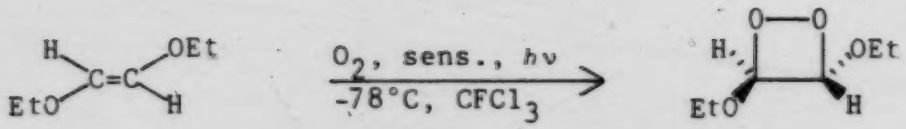
In the second route, singlet oxygen reacts stereospecifically (eq 7)[9] with electron rich olefins having no active hydrogens capable of undergoing the *ene* reaction (eq 8)[10] α-to the double bond. The third route involves treating the olefin with triphenyl phosphite ozonide to

(7a)



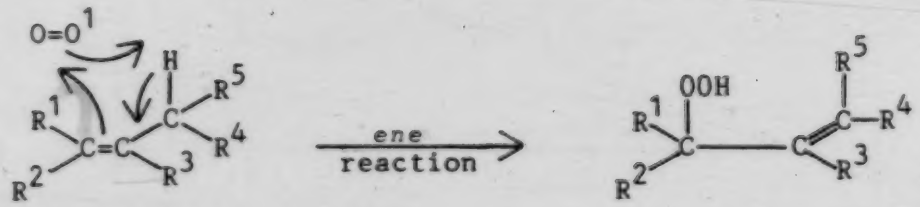
cis-5 *cis*-6

(7b)



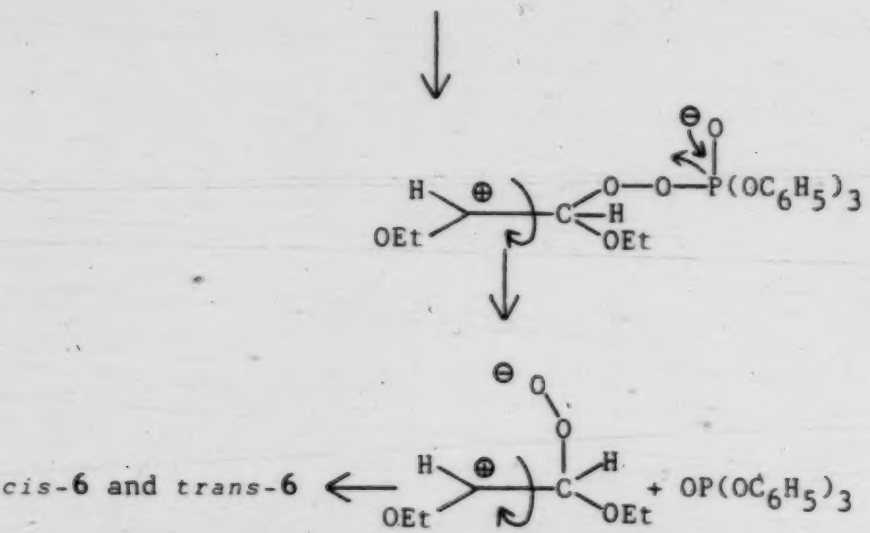
trans-5 *trans*-6

(8)



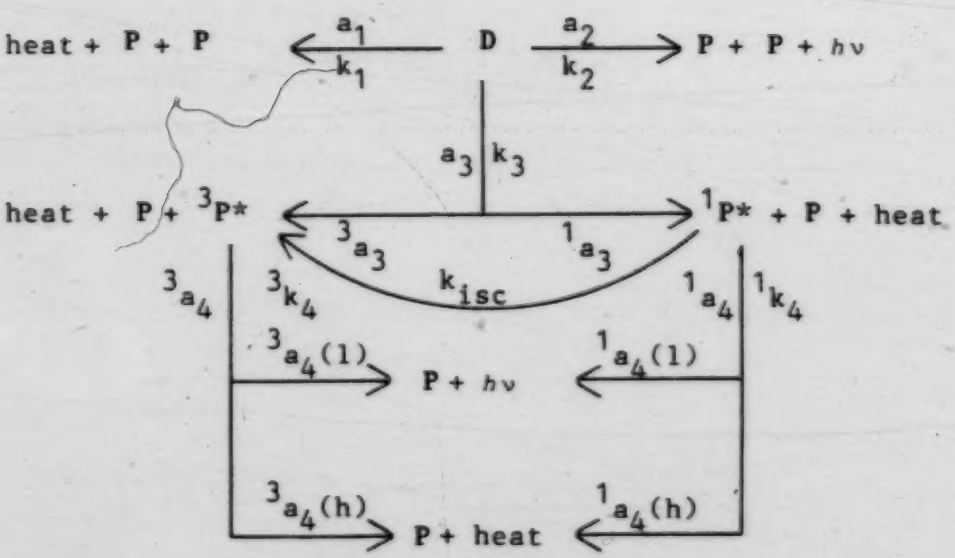
form the 1,2-dioxetane (eq 9)[11] but this takes place in a nonstereospecific manner and has not been used as generally as the first two methods. The report of a fourth route to 1,2-dioxetane by direct ozonolysis of the starting olefin in pinacolone as solvent[12] was later disproven by several authors[13,14].

cis-5 (or *trans*-5) + $(C_6H_5O)_3PO_3$ (9)



Once a 1,2-dioxetane **(D)** has been made, it could conceivably decompose to carbonyl products **(P)** by three possible paths as shown by a_1, a_2 and a_3 in Scheme I. The

SCHEME I



overall rate of decomposition, k_d, which would equal the sum of k_1, k_2 and k_3 according to this scheme, is easily measured by using either i.r. or n.m.r. spectroscopy or iodometry to follow the disappearance of **D** or the formation of **P**. The decay rate of the emitted light intensity, k_1, is even easier to measure and, because $k_4 \gg k_3$ would equal the sum of k_2 and k_3 in Scheme I. The activation energy, E_a, and the activation energy of the chemiluminescence intensity, E_{chl}, can be obtained from Arrhenius plots of k_d and k_1, respectively, measured at different temperatures. However, a more useful method for obtaining E_{chl} is to measure the initial intensity, I_1, of a dioxetane solution at temperature T_1 and the final intensity, I_2, after being cooled to temperature T_2 in a time interval sufficiently short (about 30s) that the change in dioxetane concentration is negligible[15]. This is known as the temperature drop method and gives

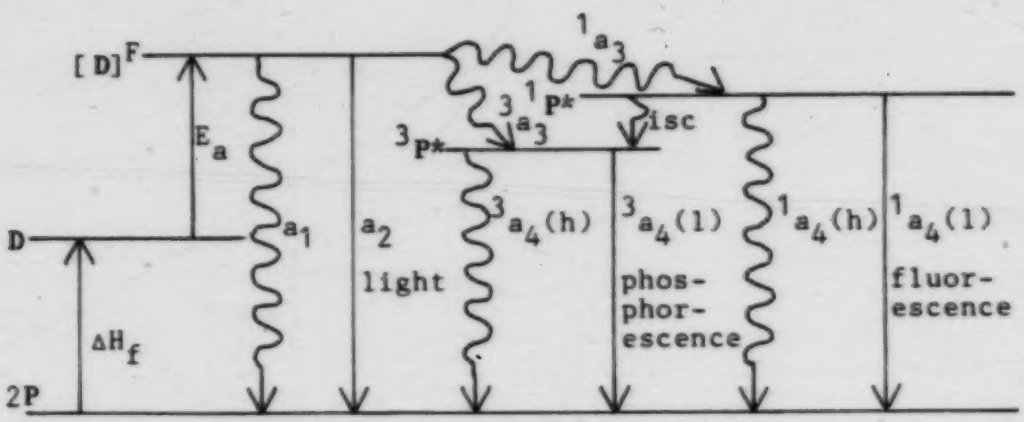
$$E_{chl} = \frac{R \ln \frac{I_1}{I_2}}{\frac{1}{T_2} - \frac{1}{T_1}}.$$

The presence of traces of transition metals[16], amines and other good electron donors[17], excited ketones (such as $^1P^*$ or $^3P^*$) and fluorescers[15,18] can catalyse the dark a_1 path and give low values of E_a and E_{chl} obtained from

Arrhenius plots. Since the dioxetane concentration does not change in the temperature drop method, catalysis of the a_1 path by impurities does not affect the value of E_{chl} obtained. The occurrence of such catalysis is thus easily detected by comparison of E_{chl} obtained by this method with E_a because $E_a < E_{chl}$. At low concentrations in pure inert solvents, pure dioxetanes show $E_a = E_{chl}$[5].

There are three lines of evidence that indicate a_3 is the major, if not the only path for light emission. The first is that upon decomposition all known **D** show the fluorescence and/or phosphorescence spectra of **P**. As illustrated in Figure I, this is expected for path a_3 but would not in general be expected for a_2. Second, when fluorescers such as 9,10-diphenylanthracene **(DPA)** or 9,10-dibromoanthracene **(DBA)** are added to solutions of **D**, the intensity of light increases dramatically. This is easily explained by path a_3. Fluorescers emit light from their singlet excited states to yield fluorescence but do not emit light from their triplet excited states to yield phosphorescence since these decompose rapidly in solution by a dark path to give heat. This is why they are called fluorescers instead of phosphorescers or excited state light emitters. The fluorescers **DPA** and **DBA** are efficient receptors of singlet and triplet energies and remove the excitation energies from the $^1P^*$ and $^3P^*$ states before they can emit heat or light by

FIGURE I



path a_4. Since these fluorescers then dispose of this captured energy to give light much more efficiently than $^1P^*$ or $^3P^*$ do by path $a_4(l)$, their addition causes the light intensity to increase. If path a_2 were the only light emitting path, it would be hard to explain how the addition of fluorescers could increase the light intensity since no excited states are generated. The only possible explanation would be for the fluorescers to catalyse the a_2 path. Wilson[19] has found that some fluorescers can catalyse the decomposition of some D with simultaneous excitation of the fluorescer. However, by measuring E_{chl} by the temperature drop method these cases are easily detected, since $E_a > E_{chl}$. In the majority of cases, $E_a = E_{chl}$ even after the addition of fluorescers and the subsequent increase in the light intensity. For these cases path a_3 must be operative. The third line of evidence for the major role of path a_3 involves measuring the yields $^1\phi$ and

$^3\phi$ of $^1P^*$ and $^3P^*$ produced. This can be done in two ways. The first uses **DPA** and **DBA** (at infinite concentration) to intercept all singlet and triplet excited states and measures the number of photons emitted by the fluorescer per mole of dioxetane decomposed. These yields, ϕ^{DPA} and ϕ^{DBA}, are easily measured on a calibrated spectrofluorometer. For both **DPA** and **DBA** an exothermic spin-allowed energy-transfer step transfers energy from $^1P^*$ or $^3P^*$ to the corresponding excited state of the fluorescer with unit efficiency. The only exception to this occurs for **DBA** in which overlap by the outer orbitals of bromine causes mixing of the singlet and triplet states allowing a certain fraction, ϕ_{TS}, of excited triplet states to transfer energy to the excited singlet state of **DBA**[20]. Because of this exception, **DBA** is well suited for measuring $^3\phi$. Since the efficiency of light production, the fluorescence yield, for **DPA** is unity and temperature independent[21], $^1\phi = \phi^{DPA}$. The fluorescence yield of **DBA**, ϕ_F^{DBA}, is less than unity (≈ 0.1) and is not temperature independent[21]. Also, ϕ_{TS} is dependent upon the structure of **P** and the solvent system used[22,23]. Thus, for very accurate measurements, ϕ_{TS} must be found for each dioxetane-solvent system being studied but when exact values are not needed, an approximation of between 0.1 and 0.3 is usually used. Since both $^1P^*$ and $^3P^*$ form excited singlet states of **DBA**, this contribution to ϕ^{DBA} must be

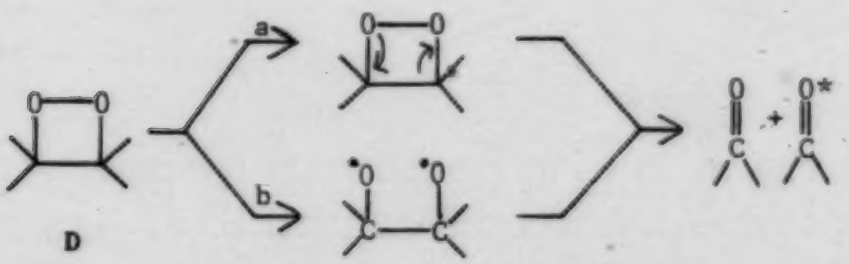
subtracted. This gives

$$ {}^{3}\phi = \frac{\phi^{DBA} - \phi_F^{DBA}\phi^{DPA}}{\phi_F^{DBA}\phi_{TS}} = \frac{\phi^{DBA}}{\phi_F^{DBA}\phi_{TS}} - \frac{\phi^{DPA}}{\phi_{TS}} \quad . $$

In normal dioxetanes ${}^{3}\phi$ is much greater than ${}^{1}\phi$ and this correction for the ${}^{1}P^{*}$ contribution to ϕ^{DBA} is usually ignored. If path a_2 is operative to some extent, then these values of ${}^{1}\phi$ and ${}^{3}\phi$ represent upper limits on the yields of excited states. The second method of measuring these yields is to react the excited states chemically with other molecules. Turro[24] found that *trans*-dicyanoethylene forms an oxetane with singlet excited states of acetone but is converted by triplet states to the *cis* isomer. Once the efficiencies for these reactions are determined by measuring the yields from ${}^{1}P^{*}$ and ${}^{3}P^{*}$ generated photochemically, it is easy to calculate ${}^{1}\phi$ and ${}^{3}\phi$ from reaction with D. To prevent the possibility of intersystem crossing, isc in Figure I or k_{isc} in Scheme I, high concentrations of olefin are used. The results of this method for tetramethyl-1,2-dioxetane (4) when compared to the method using fluorescers are identical[5]. Therefore, since the difference between the first and second methods should show the amount of light emitted by path a_2, this path is either inoperative or occurs at levels below the limit of current experimental detection.

The mechanism by which path a_3 produces excited states is the subject of much debate[3,4,5]. Any mechanism must explain how E_a and $^1\emptyset$ and $^3\emptyset$ are influenced by the structure of **D**. A selected list of these values appears in Table I. McCapra[25] first suggested that decomposition of **D** by a concerted mechanism should, according to Woodward-Hoffmann symmetry rules, proceed by a 4n anti-aromatic transition state and form one of the product molecules in an excited state (eq 10a) which would then emit light.

(10)



Kearns[26] drew a series of orbital and state correlation diagrams to explain how chemiluminiscence might occur, but these were of little predictive value. Richardson[27] first proposed an excitation mechanism in which the rate-determining step is cleavage of the O-O bond to form a 1,4-biradical (eq 10b). However, Turro[28] argued against this mechanism and to account in part for the high ratio of triplet to singlet states usually observed upon dioxetane decomposition, proposed a special spin-orbit coupling interaction as the concerted transition state was approached. This

inspired Richardson[29] to assert that the biradical mechanism could also explain the high triplet-singlet ratio and to produce evidence for this mechanism by making **7**, **8** and **9** in Table I. In a concerted mechanism, addition of phenyl groups to the dioxetane ring should stabilize the transition state and result in a lowering of E_a. The observed lack of this result in **7**, **8** and **9** is consistent with a biradical mechanism. Schuster[30] failed to find any secondary isotope effects with deuterium substitution on the dioxetane ring in *trans*-3,4-diphenyldioxetane that would be expected in a concerted mechanism. However, Wilson and Bartlett[31] made **10** and **11** and found that in comparison with **10**, **11** had an exceptionally low E_a. They also found that **11** produced only fluorescence emission. They suggest a concerted decomposition mechanism for **11** in which overlap during the transition state can occur with the singlet π,π^* state of fluorenone, while for **10**, overlap could only occur with the singlet n,π^* state which provides little transition state stabilization and leaves **10** to decompose by the normal biradical path. McCapra[32] reported that **12** forms singlet excited products with unusually high efficiency. He proposed a mechanism (eq 11) whose only difference from the chemically initiated electron-exchange luminescence (**CIEEL**) mechanism (eq 12) developed by Schuster[33,34] to explain the luminescence produced by **13** with **DPA** but not with **DBA** is that the electron

TABLE I

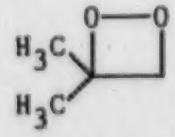
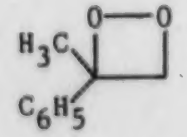
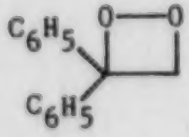
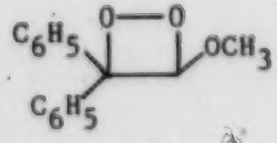
No.	Dioxetane	Solvent	E_a (kcal/mole)	$^1\phi$	$^3\phi$	Ref.
7		CCl_4	23.0			29
8		CCl_4	22.9			29
9		C_6H_6	22.7			29
10		C_6H_6	26.1±1			30

TABLE I (continued)

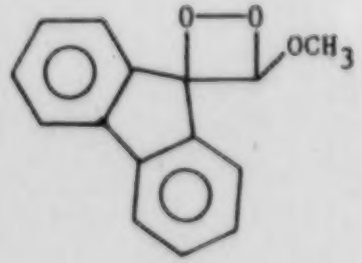
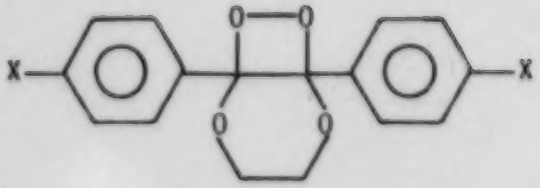
No.	Dioxetane	Solvent	E_a (kcal/mole)	$^1\phi$	$^3\phi$	Ref.
11		C_6H_6	21.0±1			30
14						
	(a) X = H	o-Xylene	24.8	1.9×10^{-4}	6.8×10^{-2}	
	(b) X = OCH_3	o-Xylene	24.0	2.4×10^{-4}	5.0×10^{-2}	35
	(c) X = $N(CH_3)_2$	$C_6H_5CH_3$	19.7±0.5	0.22	-	

TABLE I (continued)

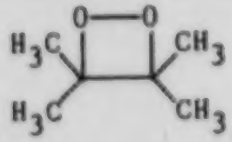
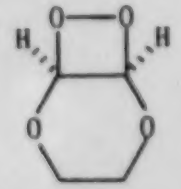
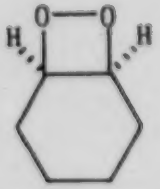
No.	Dioxetane	Solvent	E_a (kcal/mole)	$^1\phi$	$^3\phi$	Ref.
4		C_6H_5	25.6±0.3	4.4×10^{-4}	0.31	8a,41
		C_6H_6	27.6±1	.0015	0.3	37
15		C_6H_6	24.6±1	1×10^{-4}	0.3	37
cis-6		C_6H_6	24.4±1	Low	~0.2	37
16		C_6H_6	22.5±.3			38

TABLE I (continued

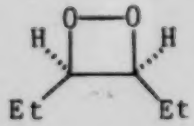
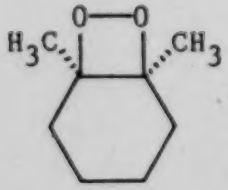
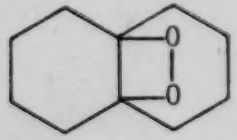
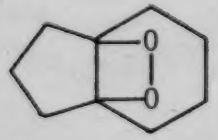
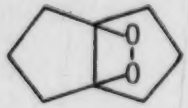
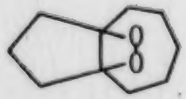
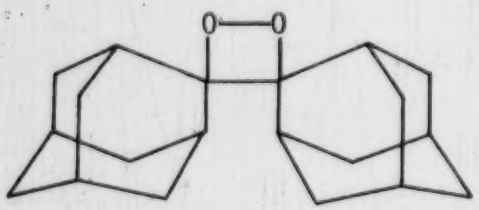
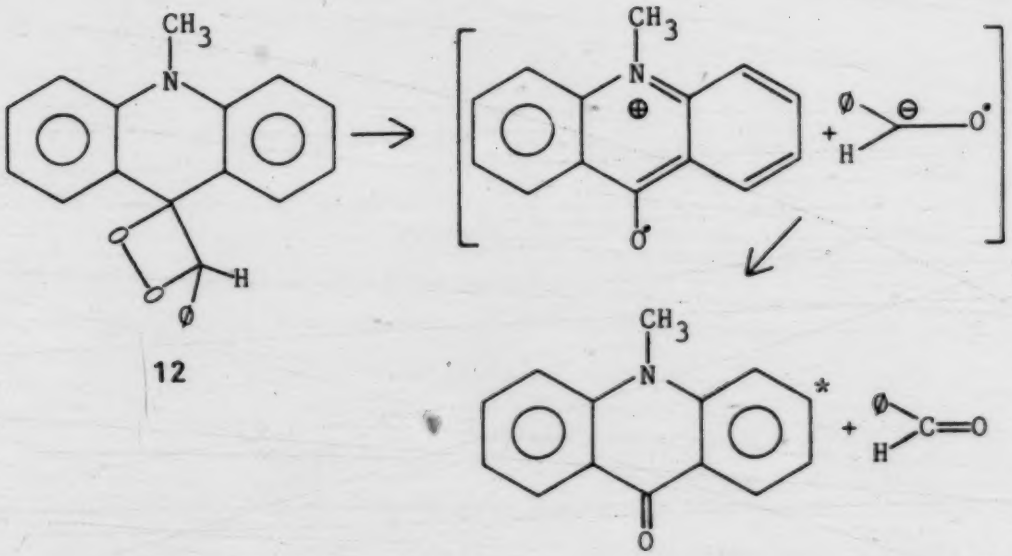
No.	Dioxetane	Solvent	E_a (kcal/mole)	$^1\phi$	$^3\phi$	Ref.
17		C_6H_6	24.5±.3			38
18		C_6H_6	24.5±1.0	8.5×10^{-4}	.23	8a,41
19		$C_6H_5CH_3$	23.0±0.6	4.8×10^{-6}	0.011	8a,41
20		$C_6H_5CH_3$	26.3±0.5	1.3×10^{-3}	0.11	40

TABLE I (continued)

No.	Dioxetane	Solvent	E_a (kcal/mole)	$^1\phi$	$^3\phi$	Ref.
21		C_6H_6	25.6±0.6	1.1×10^{-2}	0.10	40
22		$C_6H_5CH_3$	29.8±0.4	1.9×10^{-3}	0.18	40
23		Xylene	35±2	2×10^{-2}	0.15	5,42

donor and acceptor are within the same molecule. **DBA** does not produce luminescence with **13** because it has a higher ionization potential than **DPA** and cannot form $\mathbf{DBA}^{(\dot{+})}$. Wilson[19] proposed a process similar to the **CIEEL** mechanism

(11)

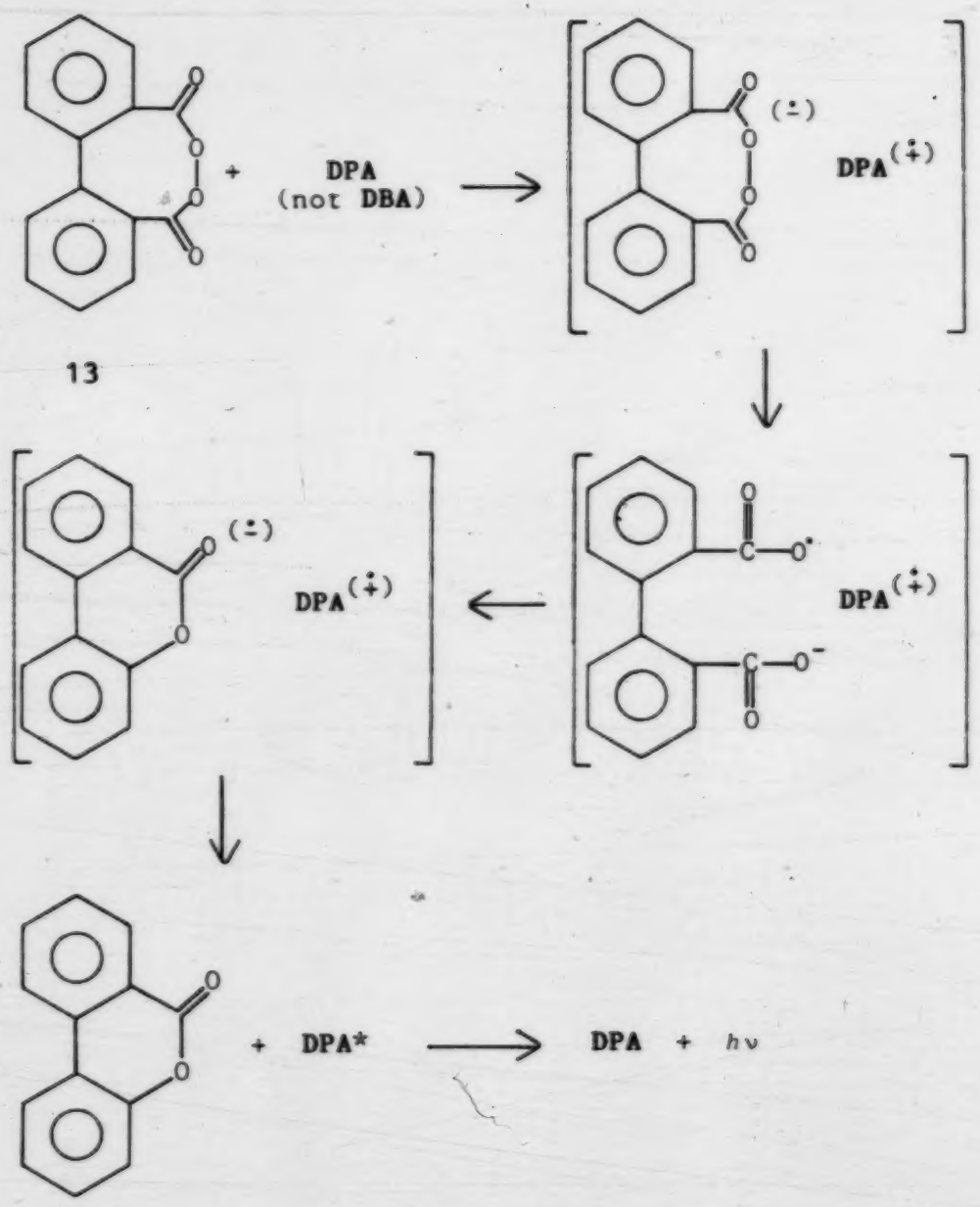


12

for the catalytic effect of fluorescers on dioxetanes in which weakening of the O-O bond in the "collision complex" occurs with simultaneous excitation of the fluorescer. Schaap[35] has invoked intramolecular electron transfer to explain the low E_a and high singlet yields of **14c** relative to **14a** and **14b**.

Fusion of the 4-membered dioxetane ring with one or more n-membered rings can create steric ring strain that

(12)

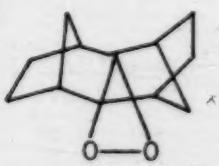


is relieved upon decomposition of the dioxetane ring. The effect this can have on E_a and $^1\emptyset$ and $^2\emptyset$ provides information about which mechanism is being followed during decomposition. *Ab initio* calculations of the reaction coordinate for 1,2-dioxetane cleavage indicate that breaking of the O-O bond is the first step[36]. Wilson compared **15** with *cis*-**6** and concluded that the release of the calculated 3-4 kcal in ring strain occurs after the transition state is reached because of their nearly identical values for E_a. However, Baumstark[38] found that **16** is less stable than **17** by 2 kcal/mole. His explanation is that

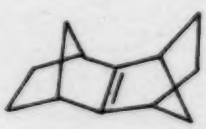
(13)

strain energy caused by the 4-membered ring distorting the shape of the 6-membered ring is relieved during the transition state if O-O stretching to form the diradical is accompanied by a twisting motion during decomposition (eq 13), thus, lowering E_a. Since **15** and **16** have about the same shape[39], this extra strain energy should be about the same for both of them. But **16** is less stable than **15** by some 0.8-3.4 kcal/mole. This could be due to stabilization of **15** by an axial oxygen atom due to an anomeric ef-

fect as suggested by Kopecky[40] or to axial interactions with the extra hydrogens contained in **16** but absent in **15**. Kopecky[40,41] investigated **18**, **19**, **20**, **21** and **22**. Comparison of the E_a values for these molecules with the value of E_a for **4** shows that E_a is average for **18**, **20** and **21**, below average for **19** and above average for **22**. The high stability of **22** results from a steric interaction that forces the hydrogen atoms attached to the carbon atoms adjacent to the bridgehead carbon atoms in the 7-membered ring closer together as the O-O bond is stretched. This effect is even more pronounced with the sterically congested **23**. Comparison of $^1\emptyset$ and $^3\emptyset$ indicates a wide fluctuation in excited yields from molecule to molecule with exceptionally low values again for **19**. No explanation can be found at present for these exceptionally low values of E_a and $^1\emptyset$ and $^3\emptyset$ for **19**[41]. In order to help find an explanation, an initial project of measuring the activation energy and excited state yields of **24** was chosen. This molecule is actually a fusion of



24



anti-**25**

19 and **21**. Inspection of molecular models shows that it is very strained and that it cannot twist as the O-O bond forms the diradical. Since all previously made 1,2-dioxetanes are capable of twisting as the diradical is formed, the triplet-singlet ratio in this molecule could reveal the extent that this twisting influences the production of excited states. Results in Table I for tricyclic 1,2-dioxetanes in which twisting should be more restricted than in the bicyclic cases indicate that a twisting motion is not necessary for the efficient production of excited states.

Unfortunately, this project of measuring the activation energies and excited state yields of **24** could not be achieved. As will be explained in more detail later in this thesis, **24** decomposed to give light immediately at all temperatures required for its formation from *B*-halohydroperoxides by treatment with either silver salts or base (eq 6). This extraordinary instability may indicate a change from a biradical to a concerted mechanism, although it could also indicate an exceptionally weak O-O bond. Most of this thesis involves the development of a new synthetic procedure for the production of olefin *anti*-**25**. This olefin could not be isolated using the published procedure of Bartlett[43] and was needed as the precursor to **24**.

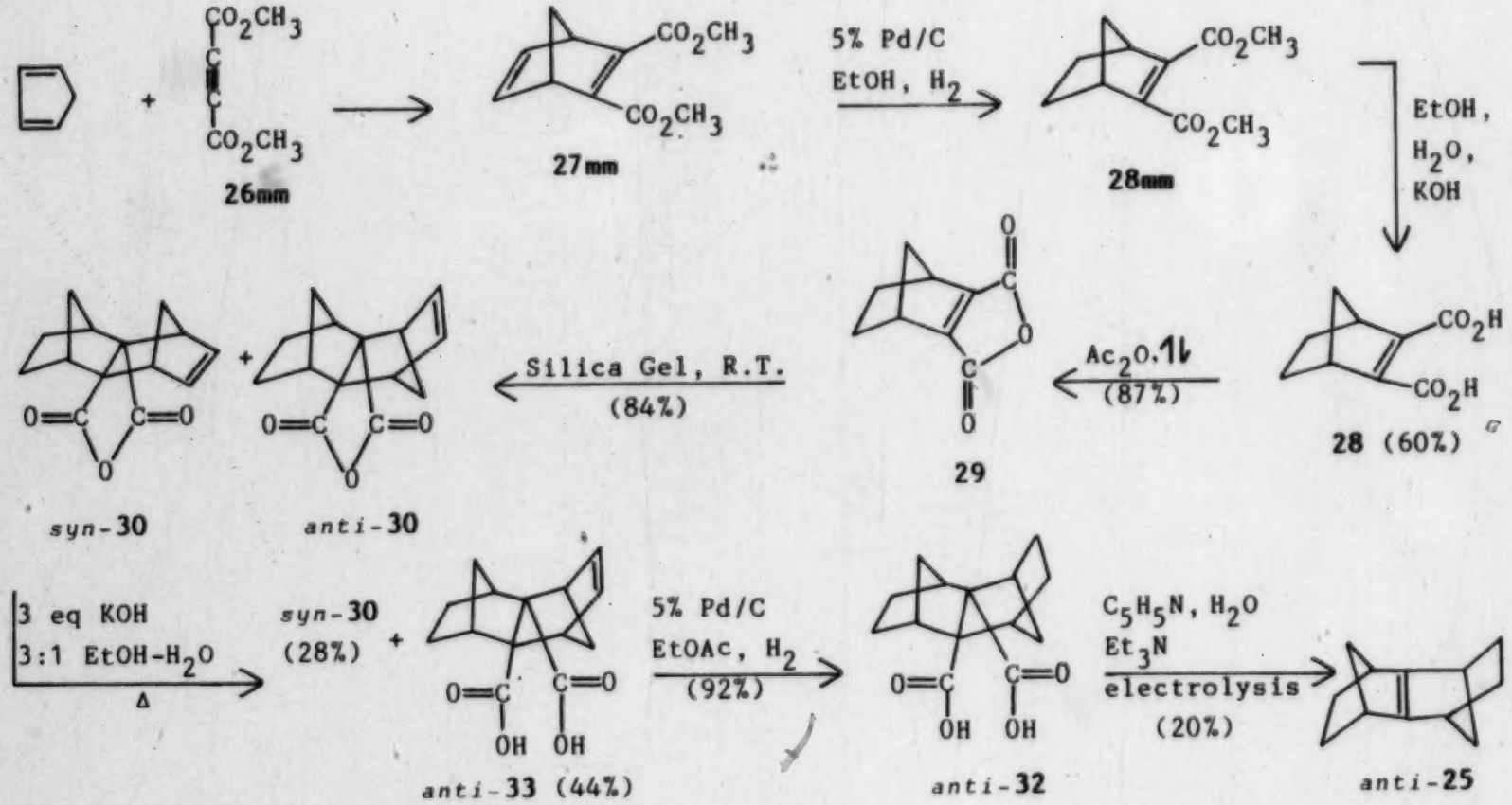
RESULTS AND DISCUSSION

Bartlett[43] has synthesized olefin *anti*-**25** in 4.1% overall yield as outlined in Scheme II. While repeating this reaction scheme, several problems, two minor and one major, were encountered that required certain modifications to be made. These modifications are outlined in Scheme III and resulted in the production of olefin *anti*-**25** in 7.6% overall yield.

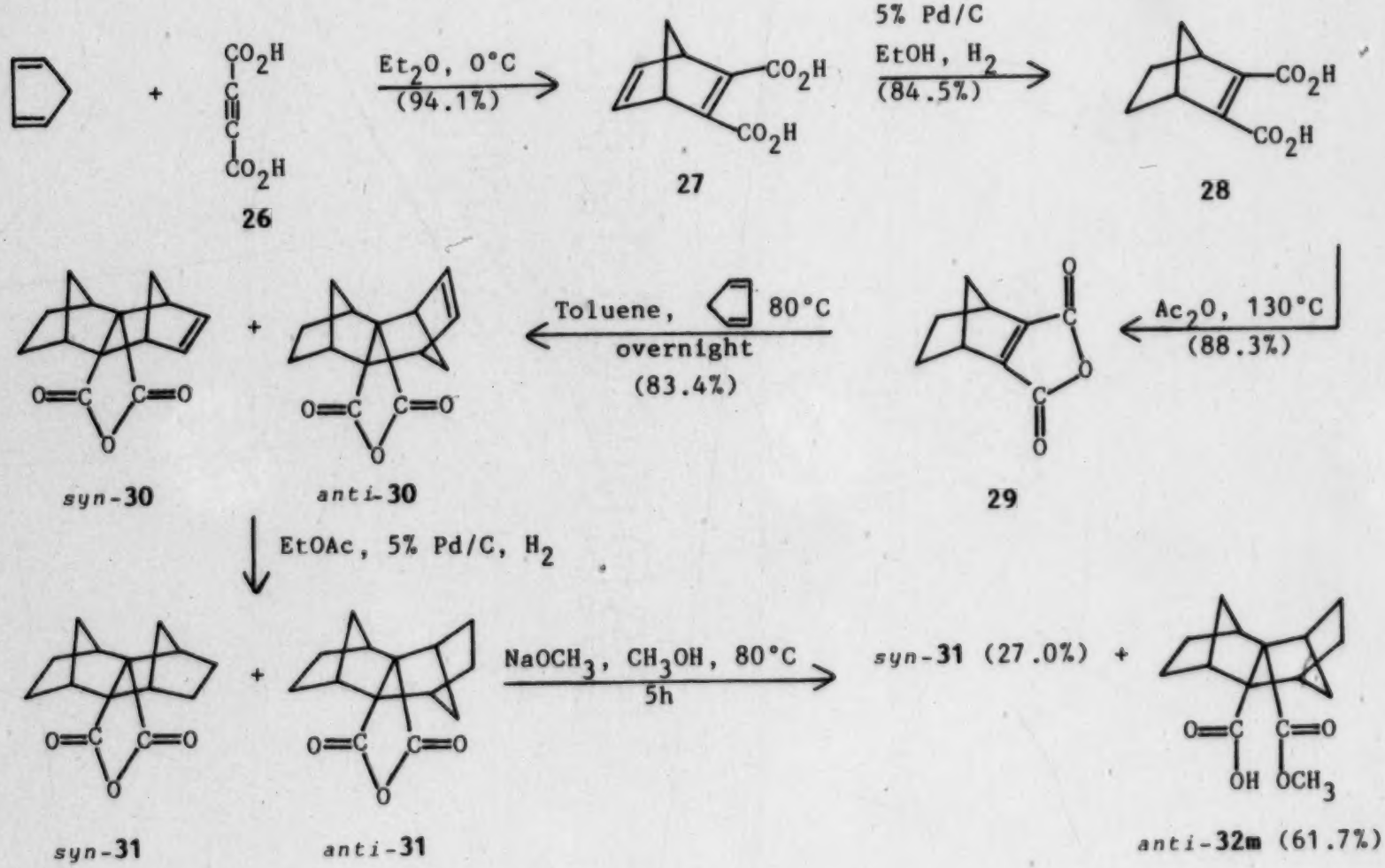
The unusual numbering system used in this thesis is a mnemonic aid for remembering monomethyl(**m**), monoethyl (**e**) and dimethyl(**mm**) esters of the parent dicarboxylic acids.

The first minor problem was that dimethyl acetylenedicarboxylate, **26mm**, was not readily available. However, acetylenedicarboxylic acid, **26**, was obtainable and could be esterified to produce **26mm**, but this reaction was inconvenient. This esterification also seemed unnecessary since the ester groups formed were subsequently hydrolyzed to produce the desired diacid **28**. The first modification, therefore, used **26** instead of **26mm** in the Diels-Alder reaction with cyclopentadiene. This reaction was performed by Diels and Alder[44] and was modified by cooling to prevent the formation of a greenish discoloration that was difficult to remove. Hydrogenation of the product, **27**, gave **28** in 79.5% overall yield as compared with Bartlett's 60%.

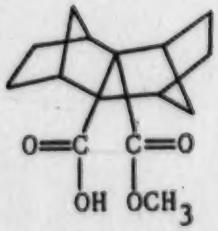
SCHEME II


26mm
27mm
5% Pd/C
EtOH, H2
28mm
EtOH,
H2O,
KOH
28 (60%)
Ac2O, 1h
(87%)
29
Silica Gel, R.T.
(84%)
syn-30
anti-30
3 eq KOH
3:1 EtOH-H2O
Δ
syn-30
(28%)
anti-33 (44%)
5% Pd/C
EtOAc, H2
(92%)
anti-32
C5H5N, H2O
Et3N
electrolysis
(20%)
anti-25

SCHEME III

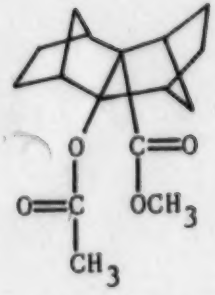

CO2H
CO2H
26
Et2O, 0°C
(94.1%)
CO2H
CO2H
27
5% Pd/C
EtOH, H2
(84.5%)
CO2H
CO2H
28
Ac2O, 130°C
(88.3%)
29
Toluene, 80°C
overnight
(83.4%)
syn-30
anti-30
EtOAc, 5% Pd/C, H2
syn-31
anti-31
NaOCH3, CH3OH, 80°C
5h
syn-31 (27.0%) +
OH
OCH3
anti-32m (61.7%)

SCHEME III (continued)



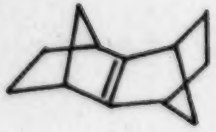
anti-**32m** (61.7%)

Benzene, AcOH, $Pb(OAc)_4$, 1h
(65.0%)*



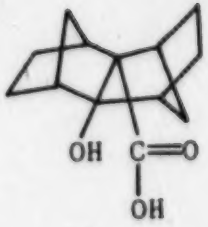
34

1h, ~10h (95%) | 1:3 H_2SO_4-H_2O



anti-**25**

C_5H_5N, Et_3N, $C_6H_5SO_2Cl$, 95°C
6h
(34%)



35

*Based on recovered starting material

The second problem encountered was also minor and involved Bartlett's use of silica gel to catalyze the Diels-Alder reaction between anhydride **29** and cyclopentadiene at room temperature. This procedure required the use of 10 g of silica gel and about 5 g of cyclopentadiene per g of anhydride **29**. When this procedure was repeated, the desired products were isolated but the silica gel developed a greenish color that was not removed by washing with chloroform or ether and had to be discarded. This procedure seemed wasteful of both silica gel and cyclopentadiene. Bartlett reported that both the uncatalyzed and $AlCl_3$-catalyzed Diels-Alder reactions were unsuccessful. In the second modification heating anhydride **29** with just a slight excess of cyclopentadiene in toluene as solvent at 80°C overnight produced a mixture of *anti* and *syn*-**30** in 83.4% yield[45], which was virtually identical to Bartlett's 84%. However, Bartlett reported the ratio of *anti* to *syn*-**30** as 1.5:1. The relative ratio of *anti* to *syn*-**30** found in several crude reaction mixtures run at different temperatures in toluene was determined by integration of the ^1H NMR absorptions at δ 6.36 and δ 6.46 due to their respective vinyl protons. These absorptions are far enough apart that fairly accurate integrations can be obtained. The results are shown in Table II. The optimum temperature for this reaction appears to be about 80°C since at 110°C less selectivity was shown for the production of the desired isomer *anti*-**30**, while at 50°C about 20%

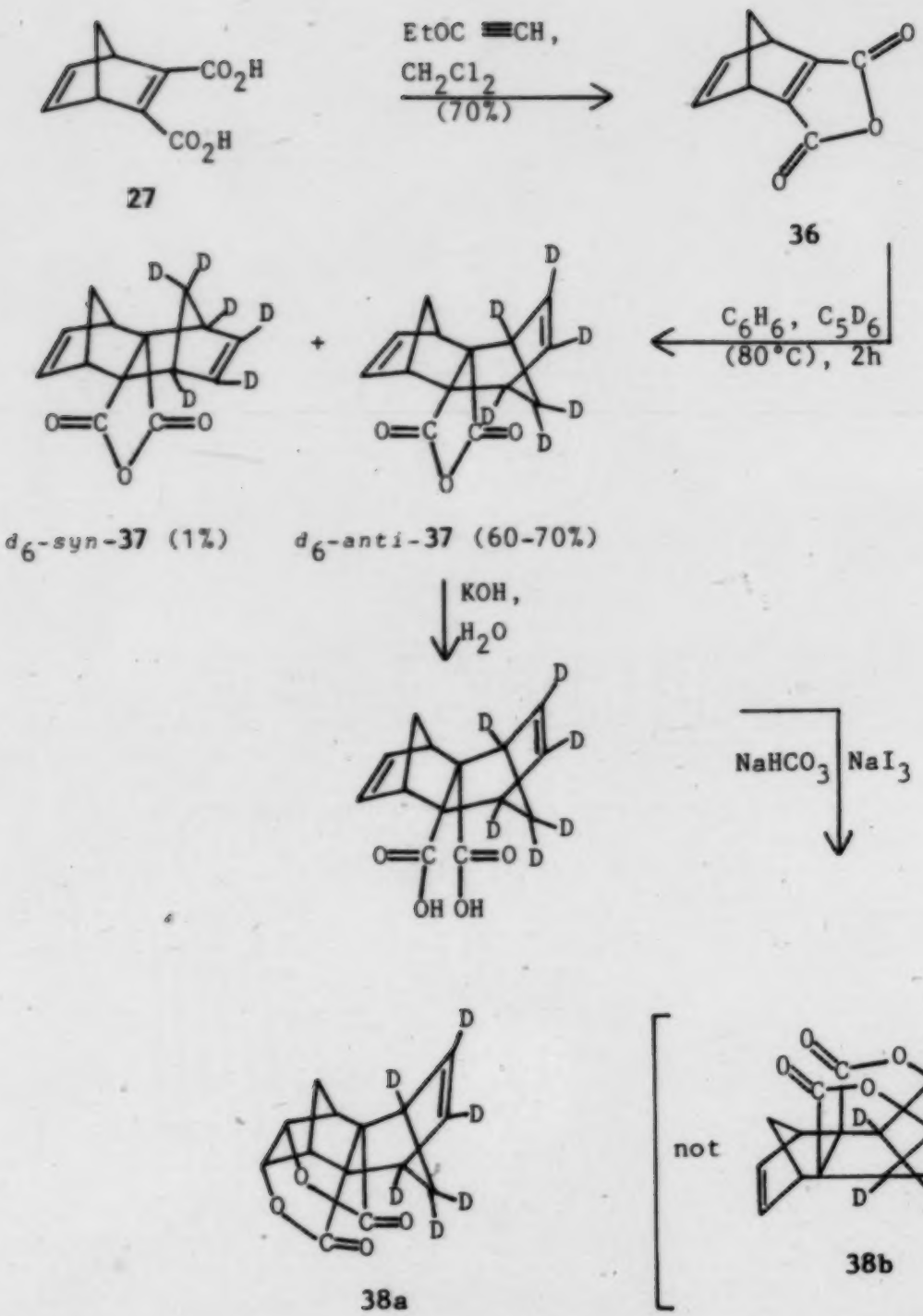
of unreacted anhydride **29** was still present in the reaction mixture even after three days. To determine if *syn* and *anti*-**30** were in equilibrium under the reaction conditions, *syn*-**30** was placed in toluene at 120°C overnight. No change was observed in the ^{1}H NMR spectrum.

TABLE II

Temp (°C)	RX. Time (h)	*anti*-**30**: *syn*-**30**
110	5	2.2:1
80	12	2.6:1
50	72	2.8:1

Four isomers are possible from this reaction. Under Bartlett's conditions using silica gel at room temperature, only two isomers were formed, the *exo,exo* isomer, *syn*-**30**, and the *exo,endo* isomer, *anti*-**30**. Bartlett determined the structures of *syn*-**30** and of *anti*-**31** made from *anti*-**30** by X-ray crystallography. The two observed isomers result from the addition of cyclopentadiene to the *exo* side of anhydride **29**. This was expected since Edman and Simmons[46] had shown by the method outlined in Scheme IV that at least 90% of the addition of cyclopentadiene to the structurally similar anhydride **36** proceeded by *exo* addition. Addition of d_6-cyclopentadiene *endo* to anhydride **36** would have produced dilactone **38b** instead of the observed dilactone **38a**. These two isomers were easily distinguished by their ^{1}H NMR spectra. For anhydride **29**,

SCHEME IV



27

36

d_6-*syn*-**37** (1%)

d_6-*anti*-**37** (60-70%)

38a

38b

additional steric hindrance by the *endo* 5,6 protons further decreases the likelihood of *endo* addition.

The difference in selectivity towards cyclopentadiene shown by the ratio of *anti* to *syn* products of 60:1 and 1.5:1 for anhydrides **36** and **29**, respectively, was noted by Bartlett who expressed surprise but offered no explanation. In both anhydrides the major product results from addition of cyclopentadiene contrary to Alder's rule. According to this rule, the p orbitals of C_2 and C_3 in cyclopentadiene would overlap the p orbitals of the carbonyl groups during the transition state to produce the *syn* isomer. Edman and Simmons[46] proposed that steric factors play a dominant role in determining the high ratio of *anti* to *syn* products produced from anhydride **36** but did not elaborate. It seems likely that steric interaction between the C_7 proton *syn* to the anhydride group in **36** and the methylene protons on cyclopentadiene would occur during addition according to Alder's rule, but would be absent during addition contrary to Alder's rule. For anhydride **29** the C_7 proton *syn* to the anhydride group may be further from the reaction site and allow addition according to Alder's rule to occur more readily.

The conversion of diacid **27** to *anti*-**37** as shown in Scheme IV followed by hydrogenation would appear to offer a better synthetic route to anhydride *anti*-**31**. However, the successful conversion of **27** to **36**, which gave poor

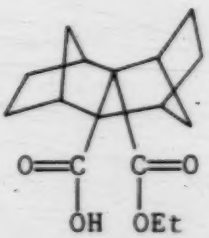
yields with all anhydrides tried and with carbodiimide[46], "depends critically on the purity of the dicarboxylic acid and ethoxyacetylene[46]." Due to the inconvenience of preparing ethoxyacetylene from diethyl chloroacetal and sodium amide in ammonia, this method was not used. The overall yield from **27** to *anti*-**37** by this method is 42-49%, while the overall yield from **27** to *anti*-**32m** shown in Scheme III is 38.4%. The two methods give approximately equal yields but the method shown in Scheme III is easier to perform.

Bartlett initially separated the mixture of anhydrides *syn*-**30** and *anti*-**30** by column chromotography and then hydrogenated each separately to the anhydrides *syn*-**31** and *anti*-**31**, respectively. However, he then found that the anhydrides *syn*-**30** and *syn*-**31** could not be hydrolyzed to the corresponding dibasic acids by treatment with hot ethanolic potassium hydroxide. Furthermore, anhydride *syn*-**31**, was stable to hot sulfuric acid and was "impervious" to attack by sodium *tert*-butyl peroxide. He suggests that this unreactivity is due to the two *syn* ethylene bridges blocking access of any nucleophile to the anhydride carbonyl groups. The anhydrides *anti*-**30** and *anti*-**31**, which have a much smaller methylene bridge in place of one of the *syn* ethylene bridges, are unable to completely block an incoming nucleophile and reacted readily with hot ethanolic potassium hydroxide to form the corresponding dibasic acids.

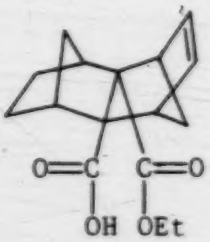
This provided a convenient method for chemically separating mixtures of *syn* and *anti*-**30** or *syn* and *anti*-**31**.

To separate a mixture of *syn* and *anti*-**30** Bartlett heated the mixture in a solution containing 3:1(v/v) ethanol-water and 3 equivalents of potassium hydroxide. Water was added to the concentrated solution and the crystals of *syn*-**30** that remained were filtered. Crystals of diacid *anti*-**33** formed upon acidifying the filtrate. To produce the desired *syn*-**31** and *anti*-**32** he then performed two hydrogenations, one on *syn*-**30** and one on diacid **33**. *Syn*-**31** and *anti*-**32** (*anti*-**32m**) were isolated with fewer manual operations by a minor modification shown in Scheme III that used a single hydrogenation to convert a mixture of *syn* and *anti*-**30** to a mixture of *syn* and *anti*-**31**, which were then separated by Bartlett's procedure. Although Bartlett did not report using this procedure to separate mixtures of *syn* and *anti*-**31**, he did report using it to convert pure *anti*-**31** to *diacid*-**32**. However, when he acidified this solution, he often obtained an oil that had to be recrystallized from ethyl acetate and did not report a yield for this reaction. When Bartlett's procedure was used to separate a mixture of *syn* and *anti*-**31**, this oil was again observed upon acidifying the filtrate that resulted from filtering the crystals of *syn*-**31**. The oil was extracted into ether and the solution evaporated to dryness. ^{1}H NMR ($CDCl_3$) of

this dry powder showed a quartet at δ 4.25. A small amount of this impurity, about 6%, was isolated as described in the experimental section and was found to result from attack by ethoxide on the anhydride group of *anti*-**31** to yield *anti*-**32e**. The most helpful of the methods used for determining the structure of this molecule were its elemental analysis, its absorption in the



anti-**32e**



anti-**33e**

^{1}H NMR at δ 4.25 (q,2H), and its mass spectrum with m/e 278 (2.4%, M^+), 260 (3.2%, M^+-H_2O), 250 (0.2%, $M^+-CH_2=CH_2$), 234 (23.0%, M^+-CO_2), 233 (22.8%, $M^+-OCH_2CH_3$), 232 (36.2%, $M^+-HOCH_2CH_3$), 212 (70.4%, $M^+-C_5H_6$) and 194 (Base, $M^+-C_5H_6-H_2O$). A small peak in the mass spectrum at m/e 279 (2.0%) was ignored and could be due to proton transfer by the acid group when the sample was injected at 200°C. Thus, in using Bartlett's procedure to produce diacid *anti*-**32** from anhydride *anti*-**31**, some *anti*-**32e** is also produced as an impurity and may be responsible for the oil that often forms during work-up. The possibility that *anti*-**33e** might be formed as an impurity from *anti*-**30**

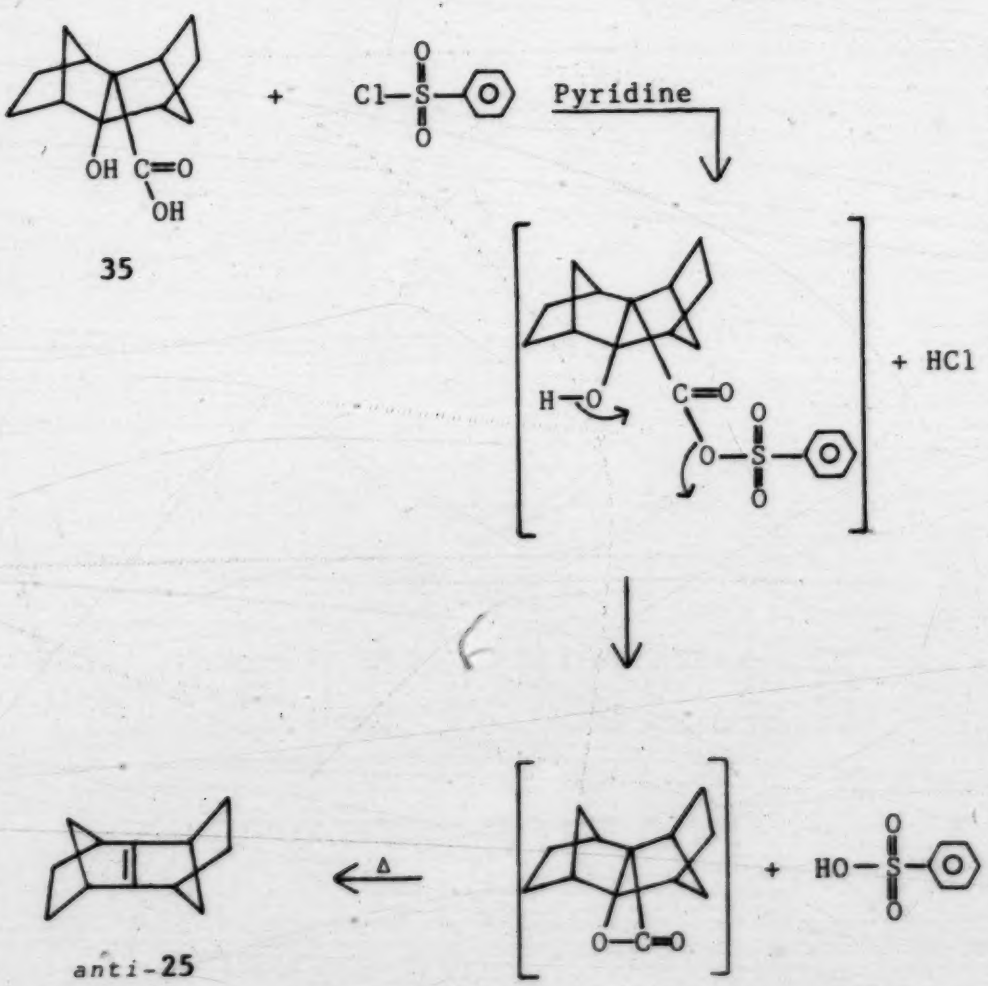
during Bartlett's separation procedure was not investigated.

The third and major problem encountered with Bartlett's scheme was that the electrolysis step converting diacid *anti*-**32** to olefin *anti*-**25** did not work when performed on the platinum gauze electrode apparatus that was available. This reaction was repeated many times at temperatures ranging from 0°C to 100°C but no trace of olefin *anti*-**25** was ever isolated. This could have been caused by insufficient voltage which was typically only about 10V when the current was 0.8A. Bartlett had reported about 50V at 0.8A. Increasing the current in an attempt to increase the voltage activated a fuse that caused all current to be lost. A short circuit between the electrodes was not present since the current dropped to zero when the reaction solution was removed. However, vigorous bubbling as described by Bartlett was observed at the anode, presumably from CO_2, and the current dropped from 0.8A to about 0.2A overnight, an indication used by Bartlett to determine that the reaction was over. Attempts to recover either the starting diacid *anti*-**32** or the anhydride *anti*-**31** yielded only a sticky black tar. Since the yield obtained by Bartlett for this reaction was only about 20% and because of the difficulty encountered in duplicating even this low yield, a new method to achieve this synthetic transformation was sought.

One of the problems with performing reactions on diacid *anti*-**32** was that it easily dehydrated to reform anhydride *anti*-**31**. For example, after it had been removed from anhydride *syn*-**31** by Bartlett's separation procedure, this acid was often extracted into ether during work-up. If all traces of mineral acid were not completely removed by washing this solution at least five times with distilled water, then anhydride *anti*-**31** was the only product recovered when the solution was evaporated to dryness on a rotary evaporator. When Bartlett attempted to perform a bisdecarboxylation reaction with this diacid or its dipotassium salt to directly form olefin *anti*-**25** by treatment with lead tetraacetate[48] and pyridine in dimethyl sulfoxide or benzene, only anhydride *anti*-**31** was recovered. Another attempted bisdecarboxylation reaction tried by Bartlett using cuprous oxide and 2,2′-dipyridyl in quinoline[49] gave the same result. Because of this dehydration problem, he then tried removing the anhydride group of *anti*-**31** by treatment with bis (triphenylphosphine) nickel dicarbonyl[50] and of *syn*-**31** by treatment with tris (triphenylphosphine) rhodium chloride[51] to form the corresponding olefins, but he observed no reaction. This was probably due to steric hindrance by the ethylene and methylene bridges *syn* to the anhydride group. His attempts to remove the anhydride group of *anti*-**31** photochemically and of *syn*-**31** thermochemically to form the corresponding olefins were also unsuccessful.

The reactions performed by Bartlett covered all known methods for removing an anhydride group to form an olefin and so a new method had to be devised. The previous isolation of the ester acid *anti*-**32e** suggested that the first step in the new method could be the removal of just one carboxylic acid group by treatment with lead tetraacetate while the other was protected as an ester group to prevent the dehydration that Bartlett had observed with the diacid using this reagent. Removal of the acid group by lead tetraacetate from a normal tertiary carboxylic acid leaves a carbocation that either eliminates a proton from an adjacent carbon to produce olefin as the major product or adds acetate to give a minor product. For this molecule the formation of an olefin would have to occur at a bridge-head position and so addition of acetate was expected to be the major path. Removal of the protecting ester group by hydrolysis to reform the acid would also hydrolyze the acetate to an alcohol. The problem would then become one of converting a *β*-hydroxy acid into an olefin. Perusal of the literature showed that Adam[52] had found a one-step procedure for this transformation using two equivalents of benzenesulfonyl chloride in pyridine at 45-55°C. The mechanism for this reaction as it would apply to hydroxy acid **35** is outlined in eq 14. Using this procedure, he reported yields ranging from 55-82%. This

(14)



35

anti-25

synthetic path that used four reactions in converting anhydride *anti*-**31** to olefin *anti*-**25** was investigated as a replacement for Bartlett's method that used two reactions.

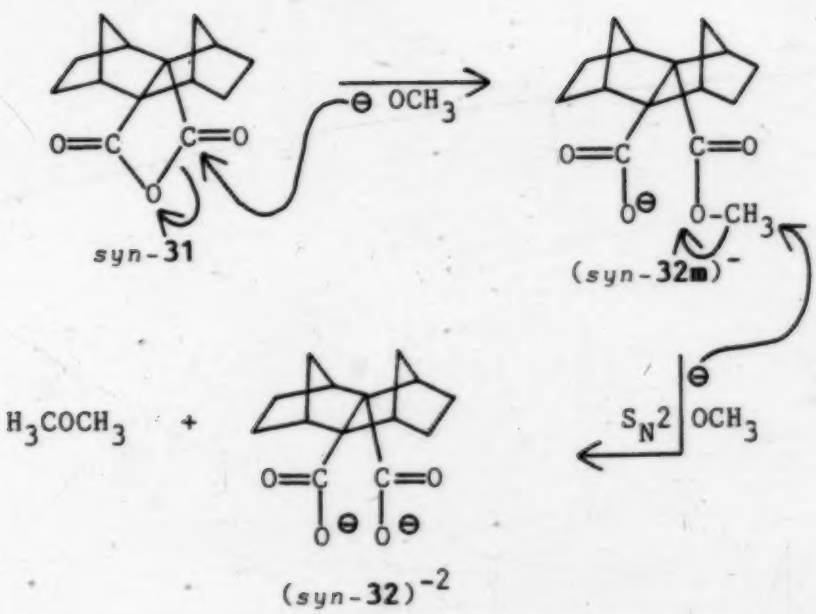
In the first reaction of this sequence the methyl ester acid *anti*-**32m** was isolated from a mixture of *syn* and *anti*-**31** in a modified version of Bartlett's procedure. In order to simplify the ^{1}H NMR spectrum the methyl ester acid was chosen instead of the previously characterized ethyl ester acid *anti*-**32e** whose triplet from the ethyl group occurred in a region already profuse with multiplets. In this new separation procedure the mixture of *syn* and *anti*-**31** was heated with about three equivalents of sodium methoxide in absolute methanol. The basic reaction mixture was then concentrated, water was added and the crystals of *syn*-**31** that remained were filtered. Acidification of the filtrate afforded the methyl ester acid *anti*-**32m**. After several hours in refluxing methanol very little reaction had occurred and almost all of the starting mixture was recovered when water was added to the concentrated reaction solution. Since *anti*-**31** had not completely reacted, the reaction was performed in a glass pressure bottle and higher temperatures and longer reaction times were tried. At this time the exact ratio of *anti*-**30** to *syn*-**30** produced in the Diels-Alder reaction between anhydride **29** and cyclopentadiene in toluene that

is shown in Table II was not known. Since Bartlett had reported that "no conditions were found under which the *syn*-saturated anhydride *syn*-**31** could be hydrolized" due to steric hindrance by the two *syn* ethylene bridges, this ratio would be determined by making sure the reaction with *anti*-**31** went to completion by using high temperatures and long reaction times and then comparing the amount of *anti*-**32m** produced to the amount of *syn*-**31** crystals isolated by filtration. As these higher temperatures and longer reaction times were tried, fewer and fewer crystals of *syn*-**31** were isolated relative to the amount of starting material. In one reaction at 120°C over the weekend the ratio of mass missing from starting mass to *syn*-**31** was about 7:1. It was "obvious" that very little *syn*-**30** was produced by the Diels-Alder reaction in toluene. However, isolation of the "missing mass" gave a powder with a wide melting point range and it was recrystallized from ethyl acetate at room temperature overnight. The pretty crystals that formed were easily identified as *anti*-**32m** by elemental analysis, the absorption at δ 3.72 (s,3H) in the ^{1}H NMR spectrum, and its mass spectrum with m/e 264 (2.9%, M^+), 246 (3.2%, M^+-H_2O), 233 (8.1%, M^+-OCH_3), 232 (8.6%, M^+-HOCH_3), 220 (34.8%, M^+-CO_2) and 198 (Base, $M^+-C_5H_6$). However, of the initial mass used for this recrystallization, less than half was recovered as *anti*-**32m**. No new crystals formed when the ethyl acetate solution

was cooled overnight at 0°C and several seeding crystals that had been placed in it did not grow. The powder isolated after the solvent had been removed had a wide melting point range that was not improved by several recrystallizations from ether-pentane, no absorptions in the ^{1}H NMR corresponding to a methyl ester, and no mass at m/e 264 in the mass spectrum. Since this powder contained side products and not the desired *anti*-**32m**, it was ignored for many months. When it was realized that the ratio of *anti* to *syn*-**30** produced by the Diels-Alder reaction in toluene had still not been accurately determined, this ratio was determined by ^{1}H NMR integration as previously described to produce the results shown in Table II. The 2.6:1 ratio determined by this method was very different from the 7:1 ratio that had been seen during chemical separation. Because of these results, some anhydride *syn*-**31**, which had accumulated over the months to a sizable quantity, was heated with sodium methoxide in absolute methanol at 150°C for two days. However, since Bartlett had shown it to be stable to boiling sulfuric acid, no reaction was expected. Thus, it was surprising when no crystals formed upon addition of water to the concentrated reaction mixture and even more surprising when the diacid *syn*-**32**, not the ester acid *syn*-**32m**, was isolated in 83% yield. This diacid showed absorptions in

the ^{1}H NMR at δ 10-5 (br, 2H) due to two carboxylic acid groups with no absorptions corresponding to a methyl ester, was pure by elemental analysis and had peaks in the mass spectrum with m/e 206 (34.1%, M^+-CO_2), 188 (6.7%, $M^+-CO_2-H_2O$), 160 (7.1%, M^+-2CO_2H), 140 (18.5%, $M^+-CO_2-C_5H_6$) and 139 (Base, $M^+-CO_2H-C_5H_6$). When the ester acid *anti*-**32m** was treated under these conditions overnight, the diacid *anti*-**32** was isolated in 87% yield and shown to be identical by mixed melting points to an authentic sample previously prepared. Finally, when 8 g of *syn*-**31** were treated with just one equivalent of sodium methoxide in absolute methanol at 150°C for just 1.5 h, 1.2 g of a mixture containing both the diacid *syn*-**32** and the methyl ester acid *syn*-**32m** was obtained. From this mixture 0.2 g of *syn*-**32m** was isolated by recrystallization from ether-pentane. This sample was pure by elemental analysis, exhibited peaks in the mass spectrum at m/e 233 (5.2%, M^+-OCH_3), 220 (43.5%, M^+-CO_2), 198 (8.7%, $M^+-C_5H_6$), 188 (25.8%, $M^+-HOCH_3-CO_2$), 160 (14.9%, $M^+-HOCH_3-2CO_2$) and 153 (Base, $M^+-CO_2H-C_5H_6$) and had an absorption at δ 3.83 (s, 3H) in the ^{1}H NMR. A mechanism consistent with these results is outlined for the *syn* anhydride in eq 15. Ingold[53] termed the S_N2 reaction bimolecular base catalyzed alkyl-oxygen fission ($B_{AL}2$). Bunnet[45] was first to report the $B_{AL}2$ mechanism in solution. He isolated both dimethyl ether and benzoic acid when he heated methyl benzoate

(15)



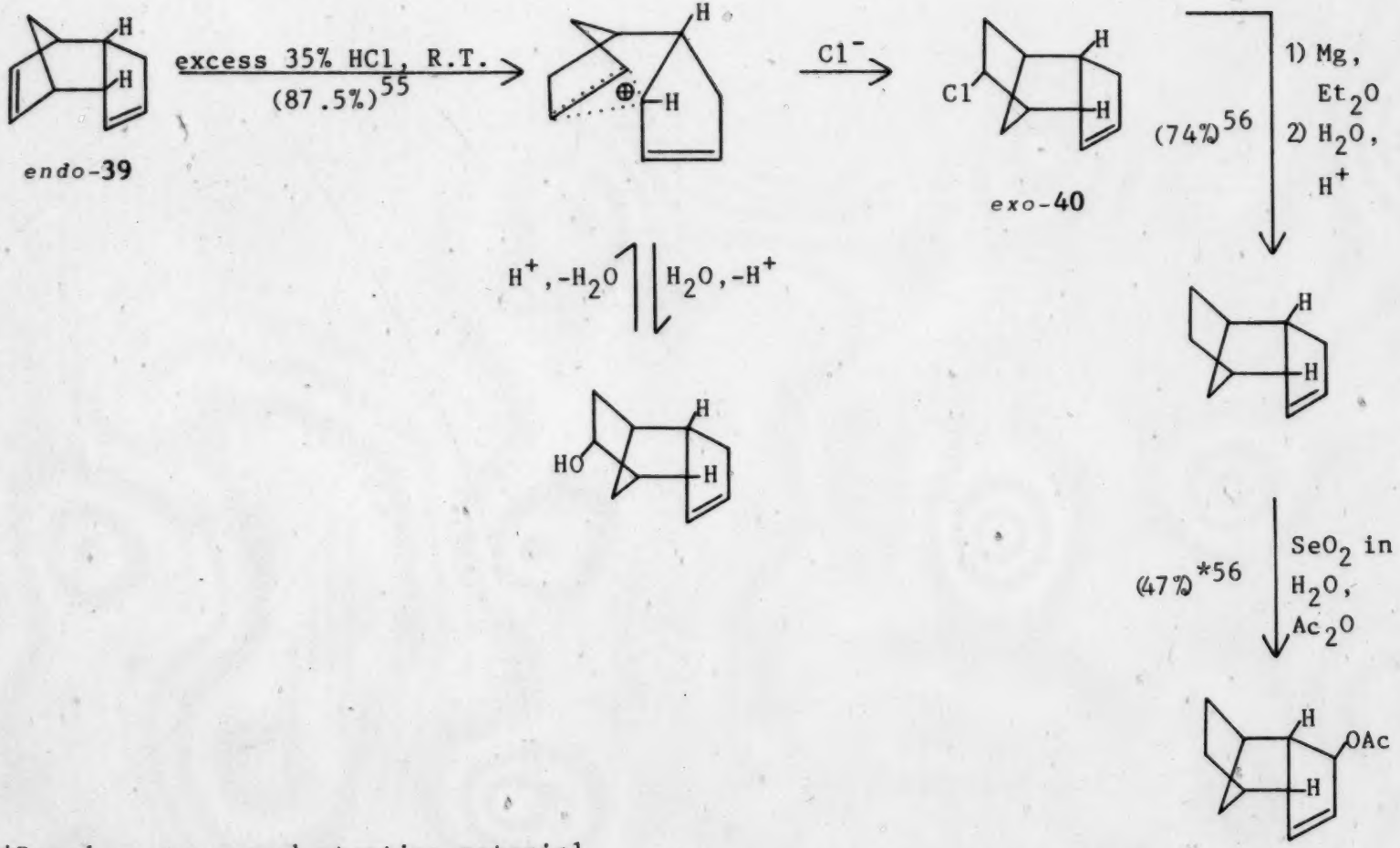
at 100°C for 55 h. For the reactions with *syn*-**31** and *anti*-**32m** no attempt was made to determine the presence of dimethyl ether. The mechanism shown in eq 15 nicely explains the unknown powder that was obtained from the ethyl acetate solution after the initial crystallization of the crude *anti*-**32m**. Under the high temperatures and long reaction times used in the separation of *syn* and *anti*-**31**, some of the *anti*-**32m** that had formed reacted again with methoxide by the $B_{AL}2$ mechanism to produce the diacid *anti*-**32**. If this had been the only diacid formed, it would have been easily identified. However, *syn*-**32** was also produced and this caused the wide melting point range that was not improved by

recrystallization in ether-pentane because of the similar physical properties of the two acids. Since both are very soluble in ethyl acetate, they remained in solution during the crystallization of *anti*-**32m**. The mass spectrum and the ^{1}H NMR spectrum of this powder are easily understood since no methyl esters were present. To minimize these reactions the separation procedure was carried out at 80°C in 5 h or less.

The isolation of *syn*-**32m** raised the interesting possibility of synthesizing olefin *syn*-**25** by the same sequence developed in converting *anti*-**32m** to olefin *anti*-**25** that is outlined in Scheme III. This olefin is currently made in 19% overall yield by the procedure shown in Scheme V[55-58]. Since determining the optimum conditions for the synthesis of *syn*-**32m** would be tedious and since it did not seem likely that a yield better than 19% would be obtained, this possibility was not investigated.

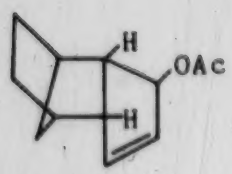
Before Bartlett reported the synthesis of olefin *anti*-**25** in 1980, the reactions outlined in Scheme V were considered as a possible synthetic route to this olefin. Alder[57] had reported that reaction of isodicyclopentadiene **41** with maleic anhydride in ether gave a quantitative yield of the anhydride *anti-endo*-**42**. Since removal of the anhydride group could be achieved

SCHEME V



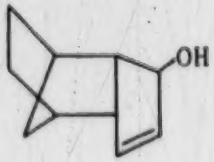
*Based on recovered starting material

SCHEME V (continued)



CH_3OH, NaOH

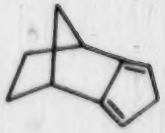
(96%)[56]



(85%)[57]

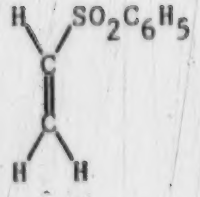
Al_2O_3

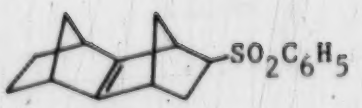
300-320°C



41

(90.7%)[58]





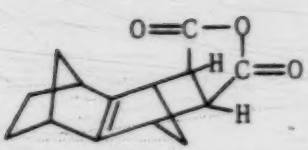
CH_3OH, $Na(Hg)_x$

Na_2HPO_4

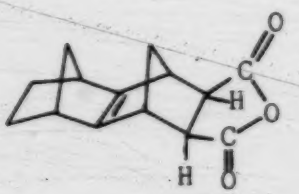
(85%)[58]

syn-25

by a number of methods, this reaction sequence offered a promising route to olefin *anti*-**25**. Much time and effort was spent performing the reactions of this sequence.



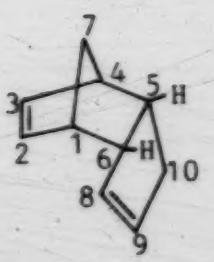
anti-endo-**42**



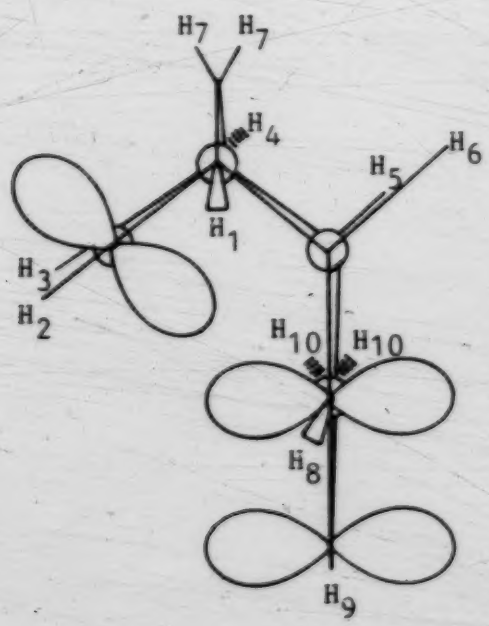
syn-exo-**42**

From a theoretical viewpoint the most interesting of these reactions was that of dicyclopentadiene *endo*-**39** with excess 35% HCl at room temperature. A Newman projection of this molecule along the C_2-C_3 and C_6-C_5 bonds is shown in Figure II. Protonation of **39** could con-

FIGURE II

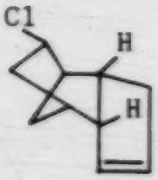


39

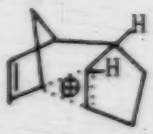


ceivably occur at either of the two double bonds to form carbocations at C_2, C_3, C_8 and C_9. These are all secondary carbocations and might be expected to have similar stabilities. However, as seen in Figure II, a carbocation at C_2 would have a vacant p orbital parallel to the adjacent C_1-C_6 bond that would allow the positive charge on C_2 to be delocalized through orbital overlap by forming intermediate **39a** shown in Scheme V. Winstein[59] first demonstrated such orbital overlap in studies on the norbornyl cation. Intermediate **39a**, which contains the norbornyl cation skeleton, explains the isolation of *exo*-**40** as the sole product from *endo*-**39**. Intermediate **39b** formed by overlap of the vacant p orbital from a carbocation at C_3

39b



40a



39c

with the parallel C_4-C_5 bond could also explain this isomerization but would produce **40a** instead of **40**. Partial

stabilization of positive charge by overlap with the C_8-C_9 π bond is possible in **39a** but not in **39b**. However, as seen in Figure II, this π bond is 30° away from being parallel to the C_1-C_6 bond and this overlap is not extensive. For this reason stabilization of a cation at C_8 by overlap of its vacant p orbital with the C_1-C_6 bond to form intermediate **39c** does not occur. No such intermediate is possible for protonation at C_9. Because of the mild reaction conditions used, protonation takes place only on the C_2-C_3 bond to form the stable intermediate **39a** and not on the C_8-C_9 bond to form the less stable secondary carbocations. As shown in Scheme V addition of water to form the alcohol can then occur but this is reversible and leads to the formation of *exo*-**40** as the sole product by the irreversible addition of chloride.

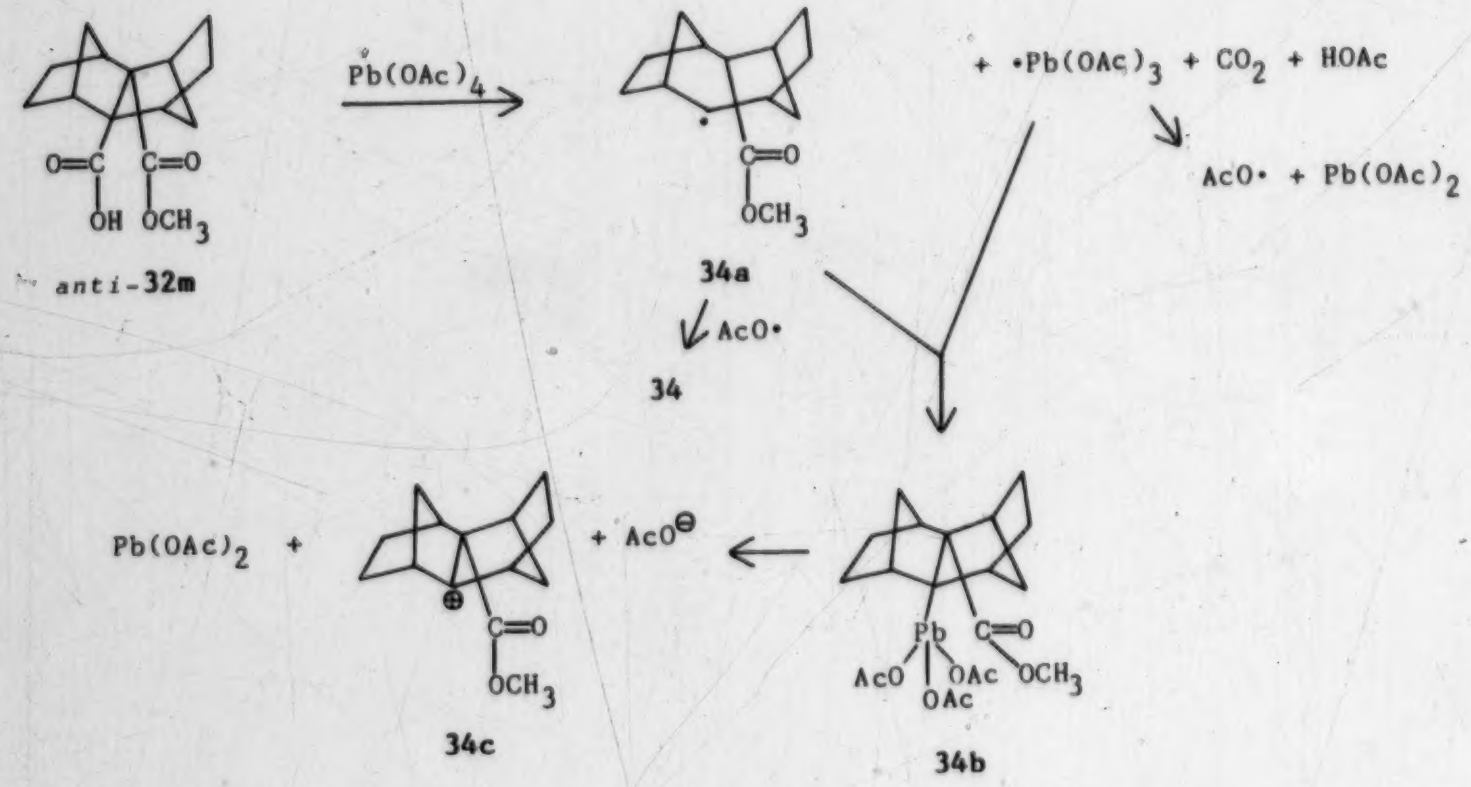
Isodicyclopentadiene **41** was prepared by the remaining sequence of reactions in Scheme V that require no special discussion and was treated with maleic anhydride. Attempts to remove the anhydride group from this product by formation of the diacid followed by treatment with lead tetraacetate in dimethyl sulfoxide produced a black sludge, presumably caused by reactions involving the central double bond. At this time Paquette[60,61] reported that the structure of this product was not *anti-endo*-**42** as reported by Alder[57] but was a 2:1 mixture of *syn-endo*-**42** and *syn-exo*-**42**. He found that maleic anhydride and

other dienophiles add to the *endo* side of **41** because of electronic, not steric, reasons and used the addition of phenyl vinyl sulfone to **41** as a key step in the synthesis of the olefin *syn*-**25** that is outlined in Scheme V. For this reason and because Bartlett had just published his procedure for the convenient synthesis of olefin *anti*-**25**, this approach was abandoned.

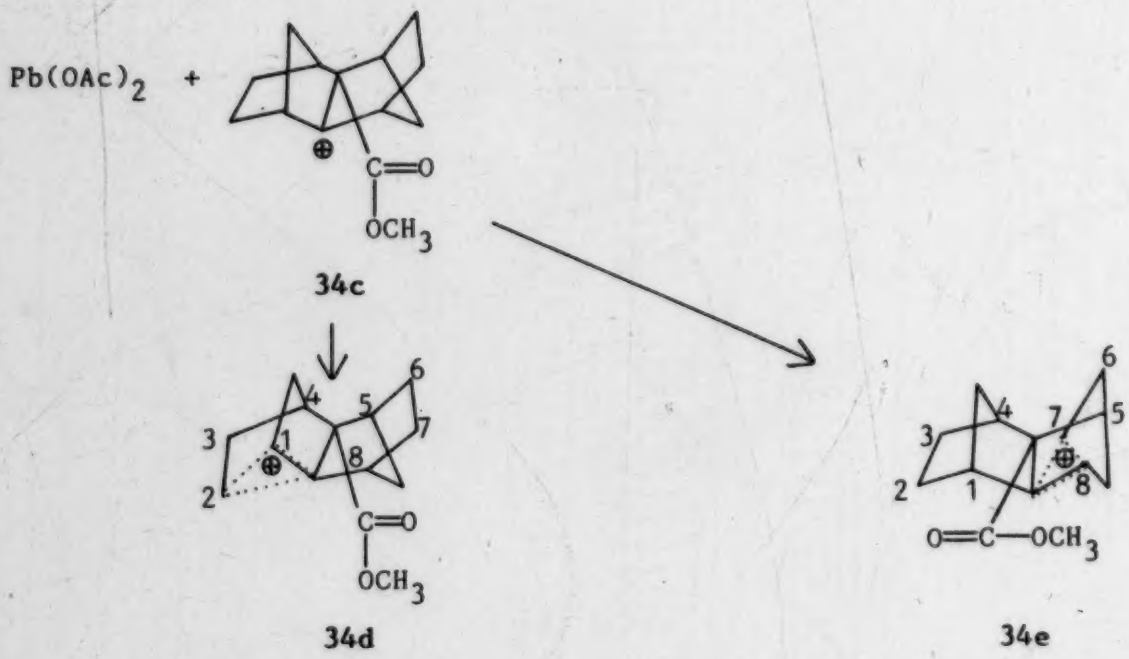
The second reaction in the new synthetic route to olefin *anti*-**25** was to remove the carboxylic acid group of ester acid *anti*-**32m** by treatment with lead tetraacetate. This reaction was performed in a refluxing solution of benzene and acetic acid. Acetic acid was present to both dissolve *anti*-**32m** and to facilitate addition of acetate to the carbocation formed by removal of the carboxylic acid group. Completion of this reaction was indicated by the disappearance of the initial yellowish color and usually took 15 to 20 h. Basic washings of this solution gave about 15% of the starting ester-acid *anti*-**32m** when acidified. Pentane was added to the dried benzene solution and a 55.6% yield (65% based on recovered starting material) of ester-acetate **34** was obtained. The structure of **34** was confirmed by its elemental analysis, its absorptions at δ 3.64 (s, 3H) from CO_2CH_3 and 2.07 (s, 3H) from $COCH_3$ in its ^1H NMR spectrum and its mass spectrum with peaks at m/e 279 (7.6%, M^++1),

278 (47.8%, M^+), 260 (12.3%, M^+-H_2O), 250 (72.3%, $M^+-CH_2=CH_2$ or CO), 247 (17.9%, M^+-OCH_3), 236 (20.8%, $M^+-O=C=CH_2$), 219 (8.1%, $M^+-CO_2CH_3$), 218 (13.0%, $M^+-CH_3CO_2H$), 212 (3.1%, $M^+-C_5H_6$), 208 (69.4%, $M^+-O=C=CH_2-(CH_2=CH_2$ or CO)), 204 (28.7%, $M^+-CH_3CO_2CH_3$), 190 (13.5%, $M^+-CH_3CO_2H-(CH_2=CH_2$ or CO)) and 176 (Base, $M^+-O=C=CH_2-CH_3CO_2H$). Further confirmation of this structure was provided by its conversion to the known olefin *anti*-**25** and is discussed later. It should be noted that addition of acetate *trans* to the ester group is sterically not possible. Attempts to obtain more than two crops of **34** from the benzene-pentane solution were unsuccessful and it was evaporated to a powder that contained 21.7% of the starting mass. This powder showed at least three overlapping spots on TLC (ether), had an ^1H NMR spectrum with strong absorptions at δ 6.5-6.3(m) belonging to vinyl protons and with almost no absorption in the region δ 2.25-1.95 belonging to acetate protons. It also showed an IR spectrum with strong absorptions from 1860 to 1650 cm^{-1} belonging to carbonyl groups and with no absorptions from 3600 to 3200 cm^{-1} belonging to an alcohol group that could result from hydrolysis of the acetate group in **34** during work-up. Although no attempt was made to identify these products, the formation of olefins containing vinyl protons can be explained as outlined in Scheme VI. The initially formed radical **34a** can

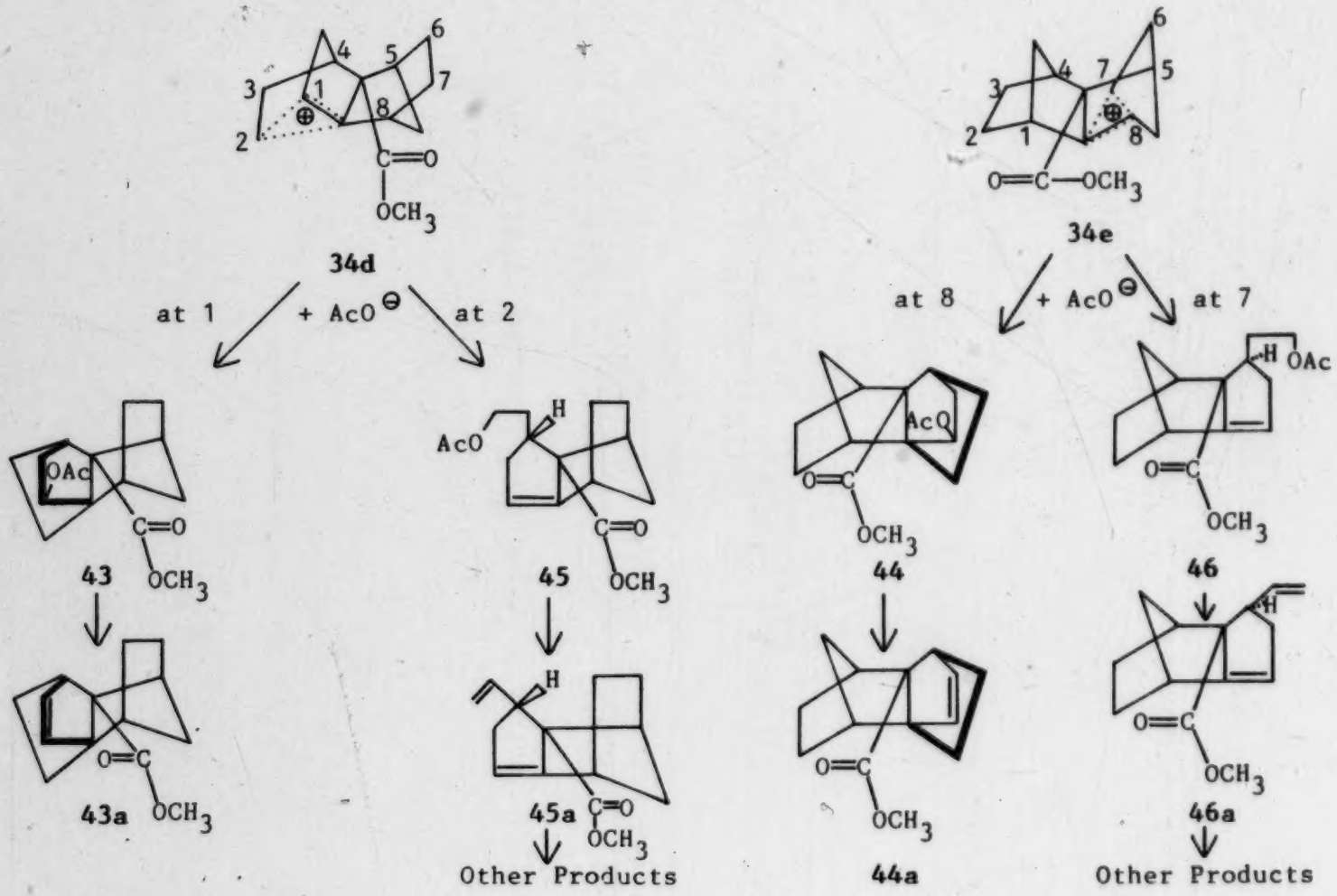
SCHEME VI


Pb(OAc)4
anti-32m
34a
+ •Pb(OAc)3 + CO2 + HOAc
AcO• + Pb(OAc)2
AcO•
34
Pb(OAc)2 +
+ AcO⊖
34c
34b

SCHEME VI (continued)



SCHEME VI (continued)

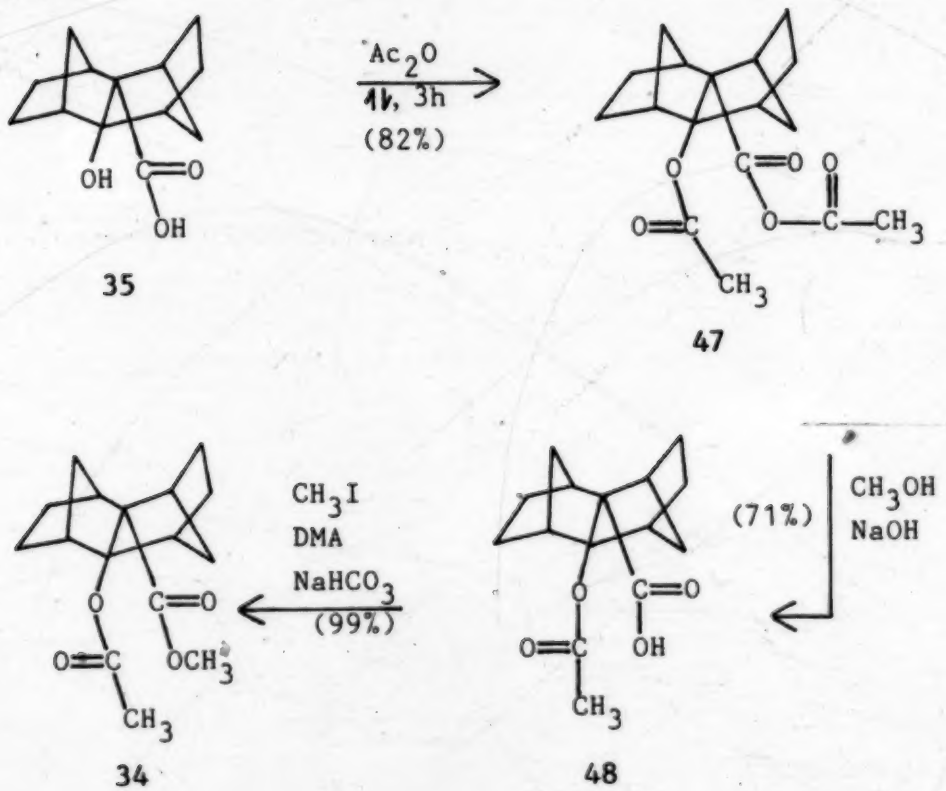


react with acetoxy radical to give **34** directly or it can be further oxidized by way of **34b** to yield the carbocation **34c**. The presence of two *trans*-fused norbornyl rings in **34c** allows the carbocation at C_{8a} to be stabilized by orbital overlap with either the C_1-C_2 bond or the C_7-C_8 bond to give rise to intermediates **34d** and **34e**, respectively.. An intermediate involving stabilization of this carbocation by simultaneous overlap with both of these bonds is an interesting possibility. Because access to the "tertiary" carbon at C_{8a} is sterically hindered, reaction of acetate could occur at "secondary" carbons C_1 and C_8 to give rise to products **43** and **44**, respectively, or at "primary" carbons C_2 and C_7 to form **45** and **46**, respectively. Elimination of acetic acid from these products yields the corresponding olefins containing vinyl protons. Subsequent migration of the double bonds in **45a** and **46a** can yield additional products.

The third reaction in the new synthetic route to olefin *anti*-**25** was to hydrolyze **34** to the acid alcohol **35**. Treatment of **34** in basic aqueous methanol was the first method tried since it was thought that acid hydrolysis would lead to rearranged products by formation of a carbocation on the carbon bearing the acetate group, but no reaction occurred at room temperature while at 95°C for 8 h an oil was produced. TLC (ether) of this oil showed many spots. Treatment of **34** with sodium methoxide

in absolute methanol at 80°C and 150°C overnight produced similar results. Since treatment with base gave impure oils, hydrolysis by acid was tried. Remarkably, treatment of **34** with 4.5 M sulfuric acid refluxing at about 130°C for about 10 h produced **35** in 95% yield! Heterogeneous reaction conditions were used to prevent any carbocation formed from reacting with any molecule other than water. These conditions had the additional benefit of signaling the end of the reaction since the entire organic phase solidified when **35**, which melts at 188-189°C, had completely formed. Using lower concentrations of sulfuric acid increased the time required for this reaction dramatically and was probably a result of both the lower proton concentration and the lower reflux temperature. The structure of **35** was confirmed by its elemental analysis, its IR spectrum showing broad absorption in the region 3500-2000 due to the acid and the alcohol groups, and its mass spectrum with peaks at m/e 222 (5.3%, M^+), 204 (13.1%, M^+-H_2O), 194 (32.6%, $M^+-CH_2{=}CH_2$ or CO), 176 (Base, M^+-HCO_2H) and 148 (45.1%, $M^+-HCO_2H, -CH_2{=}CH_2$). However, since it was hard to believe that rearrangements had not occurred under these vigorous conditions, **35** was converted back to **34** by the sequence of reactions outlined in Scheme VII.

SCHEME VII

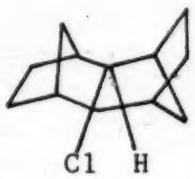


The structures of **47** and **48** were confirmed by their elemental analysis, their IR, ^{1}H NMR, and mass spectra, and their conversion to **34** which was shown to be identical to authentic **34** by ^{1}H NMR and by mixed melting point. Since rearrangements had been observed in the lead tetra-acetate reaction due to formation of intermediates **34d** and **34e**, lack of rearrangements during reaction of **34**, which would certainly form these intermediates under the much harsher conditions of 4.5 M sulfuric acid at 130°C, was surprising. This can be explained, however, if it is

assumed that such rearrangements to other products does occur, but under these conditions all of these products are in equilibrium and **35** is the most thermodynamically stable of these products. Possible reasons for this stability will be discussed later. Thus, after 10 h of equilibriation all of the initially formed side products would be converted into **35**. For the lead tetraacetate reaction such equilibriation would not occur and the side products would be isolated. This assumption would also explain the oils that were produced by treatment of **34** with base. Under the temperatures required for hydrolysis of the acetate group of **34** by base, solvolysis of the acetate group would occur with help from the C_7-C_8 bond to form intermediate **34e**. This intermediate would react with either water or methanol at either C_7, C_8 or C_{8a} to form the multiple products observed by TLC (ether). Since these reactions would be irreversible under the basic conditions, only an oil containing a mixture of products is isolated.

The final reaction in the new synthetic route to olefin *anti*-**25** was to remove the acid and alcohol groups of **35** by treatment according to Adam's procedure[52]. However, when Adam's instructions were followed and **35** was heated with two equivalents of benzenesulfonyl chloride in pyridine at 55°C overnight, the only product isolated was the highly unexpected chlorocarbon **49**. This

structure was determined by its elemental analysis and



49

by its mass spectrum that had peaks at m/e 198 (17.4%, isotopic), 196 (55.4%, M^+), 170 (9.1%, isotopic-CH_2=CH_2), 168 (28.7%, M^+-CH_2=CH_2), 161 (39.0%, M^+-Cl) and 160 (30.2%, M^+-HCl). The addition of triethylamine to this reaction gave no products at 55°C overnight but produced the desired olefin *anti*-**25** in 34% yield when carried out at 95°C for 6 h under an inert atmosphere. This olefin was characterized by its melting point of 64-65°C, identical to that reported by Bartlett, and its very clean mass spectrum with peaks at m/e 160 (20.8%, M^+), 132 (30.1%, M^+-CH_2=CH_2) and 104 (Base, M^+-$2CH_2$=CH_2).

The overall yield of olefin *anti*-**25** from acid-ester *anti*-**32m** is 21%. Bartlett reports a yield of 20% from electrolysis of diacid *anti*-**32**. However, this electrolysis procedure is limited to the production of small quantities and becomes tedious when large quantities are desired. The new procedure developed here can easily be

scaled-up to produce large amounts of this olefin in just a few days starting from the anhydride *anti*-**31**.

When olefin *anti*-**25** was treated with pyridinium hydrochloride in pyridine at 70°C overnight, chlorocarbon **49** was again isolated and shown to be identical to that isolated previously by TLC (pentane) and mixed melting point. Treatment of **49** with triethylamine in pyridine at 110°C for 8 h did not produce olefin *anti*-**25** since TLC (pentane) of this solution showed only a single spot corresponding to starting material. Thus, in Adam's reaction triethylamine acts to prevent the addition of hydrogen chloride to the initially formed olefin *anti*-**25** by acting as a proton scavenger rather than by removal of hydrogen chloride from **49** that might have been produced by some other mechanism from **35**. This appears to be the first reported addition of hydrogen chloride to a double bond by pyridinium hydrochloride. Adam did not find such a reaction to occur in any of the reactions he performed under these conditions, a review[62] of reactions with pyridinium hydrochloride makes no mention of this addition and a search of the literature up to 1981 reveals no such report.

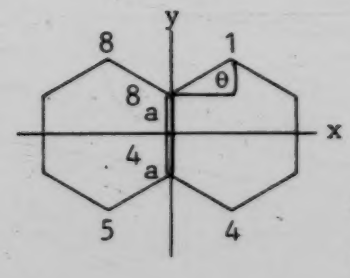
Bartlett[43] has calculated the coordinates for the carbon atoms of *anti*-**25** and some of these are reproduced in Table III. A simple trigonometric calculation from these coordinates reveals the bond angles around the

TABLE III

Atom	x	y	z
C_1	1.477	1.138	0
C_4	1.477	-1.138	0
C_{4a}	-0-	-0.690	0
C_5	-1.477	-1.138	0
C_8	-1.477	1.138	0
C_{8a}	-0-	0.690	0

central double bond as shown in Figure III. These bonds are distorted from the ideal 120° for sp^2 hybridization by 13°! This strain is relieved by the addition of hydrogen chloride since this allows the carbons at C_{4a} and C_{8a} to rehybridize to a sp^3 geometry whose ideal bond angles of 109.5° more closely resemble the 107°

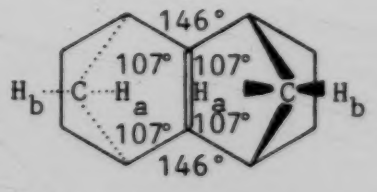
FIGURE III



$$\tan\theta = \frac{yC_1 - yC_{8a}}{xC_1}$$

$$\tan\theta = 0.303$$

$$\theta = 16.9°$$

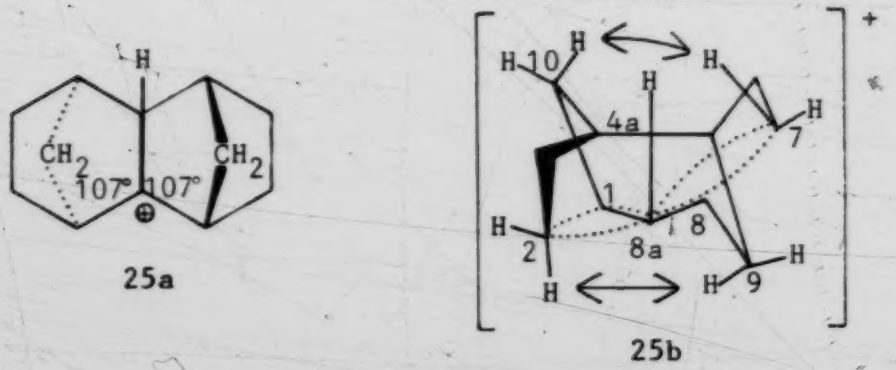


anti-**25**

bond angles imposed by the two *trans*-fused norbornyl skeletons. This addition can occur by protonation to form carbocation **25a**, which can be stabilized by orbital overlap with either the C_1-C_2 or the C_7-C_8 bond as indi-

cated by the drawing of intermediate **25b** in Figure IV, followed by the addition of chloride to C_1, C_2, C_7 or C_8 to give **49** and isomers that would be structurally similar

FIGURE IV

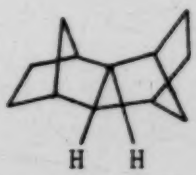


to the products **43 - 46** shown in Scheme VI. When *anti*-**25** dissolved in pentane was treated with 37% hydrochloric acid for several hours with gentle warming, an oil was obtained. This oil showed just a single spot on TLC (pentane) identical to that of **49** and had an IR spectrum also identical to **49**. Sublimation of **49** from this material was very difficult because of large amounts of a sticky substance that sublimed simultaneously. Such problems were encountered when *anti*-**25** was treated with pyridinium hydrochloride, but much less of this impurity was produced and it was removed after a few sublimations. One reason for formation of more side products in 37% hydrochloric acid might be because greater solvation of the chloride ion makes it harder for it to react with the sterically

hindered C_{8a}.

The tertiary carbocations **25a** and **34c** are exceptionally unstable for two reasons as shown in Figure IV. First, the bond angles around C_{8a} are still as strained as they were in olefin *anti*-**25**. Second, the presence of a substituent at C_{4a} induces stress imposed by the rigid geometry of the fused norbornyl skeletons that forces C_1 and C_8 to bend out of the C_{4a}-C_{8a}-C_8-C_1 plane, an effect that is similar to that which prevents formation of carbocations at bridge-head positions. Relief of this strain may be the driving force for the formation of intermediates **25b**, **34d** and **34e**. However, as indicated by arrows in Figure IV these intermediates suffer from steric interactions between protons on C_7 and C_{10} or C_2 and C_8. Earlier it was proposed that acid alcohol **35** was more stable than any of the side products that it was in equilibrium with to explain its sole formation in the reaction of **34** with boiling 4.5 M sulfuric acid. Examination of these side products shown in Scheme VI and their acid analogs shows that **45** and **46** still have an unfavorable sp^2 geometry at C_{8a} while **43** and **44** suffer from the steric congestion depicted in Figure IV. Acid-alcohol **35** may not have these steric problems and may be further stabilized by internal hydrogen bonding. Therefore, equilibrium conditions would yield it exclusively. Several reactions involving chlorocarbon **49** demonstrate the instability of a carbocation at

C_{8a}. Treatment of **49** with excess silver acetate in methanol at room temperature formed a precipitate very slowly. After several days TLC (pentane) showed that starting material was still present. An attempt was made to convert **49** into the known molecule **50**[63] by reaction with magnesium followed by treatment with water in order to conclusively prove the structure of **49**. No reaction with magnesium occurred and when 1,2-dibromobutane was added to initiate this reaction, olefin *anti*-**25**, identical by TLC (ether) and mixed melting

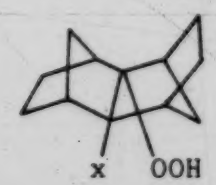


50

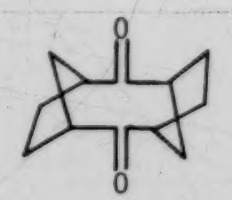
point to an authentic sample, was isolated. This provided the structural proof sought for **49**. Several other examples of the reluctance of a carbocation to form at C_{8a} will be seen shortly.

Once olefin *anti*-**25** had been made, work on production of dioxetane **24** was begun. This olefin was treated with the bromohydantoin **3b** and hydrogen peroxide in ether at 0°C as shown by eq 4 in the introduction. Work-up by washing this solution with water five or six times fol-

lowed by drying gave a solution that showed just two spots on TLC (toluene). When this TLC plate was placed on a hot plate, the slower moving spot gave off a bright light easily seen with the dark adapted eye. When some of this solution was heated on a steam bath in benzene containing fluorescer, the solution glowed brightly. Presumably this slower moving spot was the bromohydroperoxide **51a**. When heated, this molecule lost bromide to give an intermediate similar to **25a** or **25b**, formed the dioxetane with removal of the proton by bromide ion and emitted light when the dioxetane decomposed. Re-



51a, x = Br
51b, x = I



trans-**52**

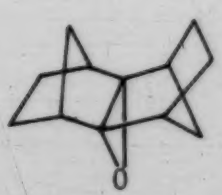
actions aimed at producing the dioxetane directly by treatment of the crude bromohydroperoxide **51a** with silver acetate or silver nitrate in methylene chloride or methanol failed at room temperature, gave off no light and showed the presence of starting material 24 h later by TLC (toluene). The iodohydroperoxide **51b** was then prepared by reaction of olefin *anti*-**25** with the

iodohydantoin **3c** and hydrogen peroxide in ether at -20°C. Work-up by washing this solution with water and then 5% sodium thiosulfate to remove iodine that had formed during this reaction followed by drying, gave a solution that also showed two spots on TLC (toluene). Light was again emitted from the slower moving spot when this TLC plate was heated on a hot plate. Small portions of this solution in dichloromethane containing added fluorescer were kept at room temperature, 0°C and -20°C while silver acetate was added and the solutions observed with the dark adapted eye. The solution at room temperature gave off a bright light, that at 0°C gave off a light that was just visible, and that at -20°C gave off no visible light. The solution at room temperature continued to glow for over eight hours while the solutions at lower temperatures were decanted from the settled silver acetate and transferred to new test tubes after thirty minutes. When these solutions were allowed to warm up to room temperature, no light was visible that would have showed a build-up of dioxetane **24**. Addition of fresh silver acetate to these solutions at room temperature caused them to emit light that lasted for many hours. If a room temperature solution was decanted from the settled silver acetate, it stopped glowing immediately but glowed again when fresh silver acetate was added. Solutions that did not contain fluorescer were allowed to stop glowing, and then evapora-

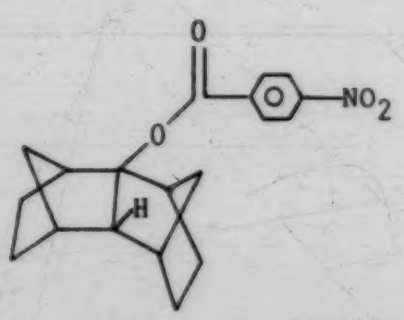
ted to dryness. The remaining silver salts were extracted with ether and the ether was evaporated to yield a residue. Sublimation of this residue gave a very small amount of *trans*-**52** that was identified by its IR spectrum which contained a strong absorption at 1665 cm^{-1} and its mass spectrum with m/e 192 (13.6%, M^+). Paquette[58] has made *cis*-**52** and its absorption in the IR at 1678 cm^{-1} compare well with that of *trans*-**50**. This low frequency of absorption may be due to a straightening of the C-CO-C bond angle of the carbonyl groups caused by structural constraints. The sample of *trans*-**52** isolated was impure as shown by its wide melting point range and several small peaks at m/e 278 (0.8%), 235 (2.2%) and 208 (1.2%) in the mass spectrum. However, the unusually low absorption frequency for this molecule in the IR is sufficient to verify its formation during these reactions and thus prove the formation of dioxetane **24** as the intermediate responsible for light production. Since this dioxetane decomposed at any temperature required for it to be formed from the bromo- or iodohydroperoxide precursors, it could not be isolated. Either dioxetane **24** has an exceptionally low E_a, possibly indicating a change from a biradical to a concerted mechanism of decomposition, or it is very sensitive to catalytic decomposition by Ag^+. However, since this latter process usually proceeds without light emission, it is

unlikely.

Other methods could be tried to produce dioxetane **24**. Bartlett[43] reported that treatment of olefin *anti*-**25** with singlet oxygen as described by eq 7 in the Introduction produced only the epoxide **53**. Treatment of olefin *anti*-**25** with triphenyl phosphite ozonide at -78°C as described by eq 9 in the Introduction, may produce *anti*-**25** at a temperature low enough for it to be isolated. However, steric problems may prevent initial reaction of the olefin with bulky ozonide at this low temperature. Paquette[58] reports that **54** has a rate of solvolysis 3.5×10^6



53



54

times faster than *tert*-butyl *p*-nitrobenzoate which he attributes to extreme steric compression. Substitution of a bulky group such as *p*-nitrobenzoate for X in **49** might allow formation of dioxetane **24** at a temperature low enough for it to be isolated before it can decompose. However, these possible methods for the production of dioxetane *anti*-**25** were not attempted and measurements of E_a, $^1\emptyset$ and $^3\emptyset$ for dioxetane **24** were precluded.

EXPERIMENTAL

Potassium hydrogen acetylene dicarboxylate was obtained from the Aldrich Chemical Co. Dicyclopentadiene was obtained from the Eastman Kodak Co. and was used to prepare fresh cyclopentadiene. Reagent grade methanol containing 0.10% water was obtained from American Chemicals Ltd. Both 1,3-dibromo-5,5-dimethylhydantoin and 1,3-diiodo-5,5-dimethylhydantoin were obtained from Arapahoe Chemicals (a division of Syntex Corp.). All other solvents and reagents were obtained from various suppliers and were usually used without further purification. The exceptions to this were pyridine, which was freshly distilled from calcium hydride, and benzenesulfonyl chloride, which was distilled. Infrared spectra (Nujol) were taken on a Perkin-Elmer 457 spectrophotometer. Infrared spectra (film) were taken on a Perkin-Elmer 421 spectrophotometer. ^{1}H NMR spectra were obtained from a Varian A56/60A analytical spectrometer. Mass spectra were taken on an AEI MS50 mass spectrometer with an electron impact energy of 70 electron volts. Melting points are uncorrected and were taken on a Gallenkamp capillary melting point apparatus. All TLC plates were made of silica gel supplied by E. Merck and Co. and were developed with iodine.

All organic extracts were shaken with saturated sodium chloride before being dried over $MgSO_4$ unless indicated otherwise.

Bicyclo [2.2.1] hept-2,5-diene-2,3-dicarboxylic Acid (27). Diacid **27** was made by an adaptation of the procedure of Diels and Alder[44]. A solution of potassium hydrogen acetylenedicarboxylate (100 g, 0.657 mol) added to a cold solution of concentrated sulfuric acid (60 mL) in water (100 mL) was extracted with ether (5 X 100 mL). Each ether extract was washed with water (1 X 10 mL) and then saturated sodium chloride solution (1 X 10 mL). These washings were then returned to the aqueous solution for the next extraction. Cyclopentadiene (66 g, 1.0 mol) was added to a stirred solution of the combined ether extracts at 0°C. Failure to cool the ether solution resulted in the formation of a dark green discoloration that was difficult to remove. The reaction mixture was allowed to warm to room temperature overnight. It was then shaken with cold 3 M sodium hydroxide (400 mL). The aqueous layer was acidified with 5 M H_2SO_4 (150 mL) and extracted with ether (3 X 200 mL). The combined extracts were washed with water and dried. The solution was concentrated to about 150 mL and pentane (300 mL) added. The crystals that formed were removed by filtration to yield 111.4 g (94.1%) of diacid **27**, mp 167-169°C (lit. 170°C)[44].

Bicyclo [2.2.1] hept-2-ene-2,3-dicarboxylic Acid (28). A solution of diacid **27** (111.0 g, 0.6163 mol) in 95% ethanol (600 mL) was hydrogenated in 200 mL portions at 10-30 psi in a Parr shaker apparatus using 5% Pd/charcoal as catalyst. The catalyst was removed by filtration, the combined portions were concentrated to about 100 mL and pentane (200 mL) was added. The crystals that formed were removed by filtration to yield 67.1 g of diacid **28**, mp 206-208°C (lit. 213-214°C)[43]. The filtrate was concentrated to an oil and a boiling solution of 1% sulfuric acid (300 mL) was added. This was done to hydrolyze any ethyl esters that may have formed during the hydrogenation in ethanol. This solution was cooled at 2°C overnight and the crystals removed by filtration to yield an additional 27.7 g of **28**, mp 205-8°C, for a total yield of 94.8 g (84.5%).

Bicyclo [2.2.1] hept-2-ene-2,3-dicarboxylic Anhydride (29). Anhydride **29** was made by an adaptation of the procedure of Diels and Alder[44]. Acetic anhydride (200 mL) and diacid **28** (67.1 g, 0.368 mol) were heated at 130°C for 1.5 h. The solution was concentrated to an oil, pentane (150 mL) was added and the crystals that formed were removed by filtration to yield 50.6 g of anhydride **29** mp 96-98°C (lit. 98-99°C)[44]; ^{1}H NMR ($CDCl_3$) δ 3.50 (s, 2H), 2.35-1.90 (m, 3H), 1.85-1.65 (m, 1H), 1.50-1.15 (m, 2H). A second crop was obtained that yielded an additional 2.7 g of anhydride **29**, mp 96-89°C, for a total yield of 53.3 g (88.3%).

1,2,3,4,4a,5,8,8a-Octahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a,8a-dicarboxylic Anhydride (*anti*-30) and 1,2,3,4,4a,5,8,8a-Octahydro-1,4:5,8-*exo,exo*-dimethanonaphthalene-4a,8a-dicarboxylic Anhydride (*syn*-30). Anhydride **29** (50.5 g, 0.308 mol), toluene (300 mL) and then cyclopentadiene (30 g, 0.45 mol) were placed in a glass pressure bottle and heated at 80°C overnight. The solution was then filtered to remove some sediment and concentrated to an oil. Pentane (150 mL) was added and the crystals that formed were removed by filtration to yield 59.2 g (83.4%) of a mixture containing *syn* and *anti*-**30**.

1,2,3,4,4a,5,8,8a-Octahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a,8a-dicarboxylic Acid (*anti*-33) and *syn*-30. Bartlett's[43] procedure was followed for this reaction. A mixture of *syn* and *anti*-**30** (29.0 g, 0.126 mol) in a solution containing potassium hydroxide (22 g, 0.38 mol), water (35 mL) and ethanol (100 mL) was heated on a steam bath for 1.5 h. The mixture was then evaporated to dryness, water (100 mL) was added and the crystals that remained were removed by filtration to yield 4.5 g (16%) of *syn*-**30**, mp 190-192°C (lit. 191-193°C)[43] with ^{1}H NMR ($CDCl_3$) absorptions identical to those in the literature[43]. The filtrate was acidified with cold 3 M hydrochloric acid (130 mL) and extracted with ether (2 X 150 mL). The combined ether extracts were washed with water (4 X 20 mL) and dried.

This solution was evaporated to dryness and the solid recrystallized from ethyl acetate (300 mL) overnight. The ethyl acetate was decanted from the crystals to yield 10.0 g (31.7%) of diacid *anti*-**33**, mp 110-113°C (d) (lit. 110-30°C (d))[43].

***Anti*-30 from *anti*-33.** Diacid *anti*-**33** (2.0 g, 8.1 mmol) in acetic anhydride (30 mL) was heated on a steam bath for 1 h. This solution was concentrated to an oil which was then dissolved in ethyl acetate (25 mL). Pentane (25 mL) was added and the crystals that formed were removed by filtration to yield 1.4 g (75%) of anhydride *anti*-**30**, mp 198-200°C (lit. 197-199°C)[43] with ^{1}H NMR ($CDCl_3$) absorptions identical to those in the literature[43].

Test for Equilibrium Between *syn* and *anti*-30. A solution of anhydride *syn*-**30** (1.1 g) and toluene (11 g) was placed in a glass pressure bottle and heated at 120°C overnight. The solvent was then removed and the residue showed no trace of *anti*-**30** in the ^{1}H NMR (C_6D_6) spectrum which was identical to that of the starting anhydride.

Relative Ratios of *anti* to *syn*-30 Produced at Different Temperatures. Three solutions containing anhydride **29** (0.33 g), toluene (2.0 g) and cyclopentadiene (0.25 g) were prepared in glass pressure bottles. One was kept at 110°C for 5 h, one at 80°C for 12 h and the last at 50°C for 72 h. They were then concentrated to

oils, benzene (20 mL) was added and they were evaporated to dryness. ^{1}H NMR ($CDCl_3$) integration of the absorptions due to the vinyl protons of *anti*-**30** and *syn*-**30** at δ 6.36 and δ 6.46, respectively, gave the relative ratios that appear in Table II. Since these molecules show no absorptions in the region δ 2.35-1.90, comparison of the integration of the absorptions due to vinyl protons (2H) with the integration of the absorptions in the region due to anhydride **29** (3H) was used to determine that about 20% of the starting material was still present in the 50°C reaction.

1,2,3,4,4a,5,6,7,8,8a-Decahydro-1,4:5,8-*exo*-*endo*-dimethanonaphthalene-4a,8a-dicarboxylic Anhydride (*anti*-31) and 1,2,3,4,4a,5,6,7,8,8a-Decahydro-1,4:5,8-*exo*-*exo*-dimethanonaphthalene-4a,8a-dicarboxylic Anhydride (*syn*-31). A crude mixture of anhydrides *syn* and *anti*-**30** (59.2 g, 0.257 mol) in ethyl acetate (250 mL) was hydrogenated at 10-40 psi in a Parr shaker apparatus using 5% Pd/charcoal as catalyst. The catalyst was removed by filtration and the solution evaporated to dryness to yield 59.5 g (99.6%) of a mixture containing *syn* and *anti*-**31**.

Ethyl Hydrogen 1,2,3,4,4a,5,6,7,8,8a-Decahydro-1,4:5,8-*exo*,*endo*-dimethanonaphthalene-4a,8a-dicarboxylate (*anti*-32e), 1,2,3,4,4a,5,6,7,8,8a-Decahydro-1,4:5,8-*exo*,*endo*-dimethanonaphthalene-4a,8a-dicarboxylic Acid (*anti*-32) and *syn*-31. A mixture of *syn* and *anti*-**31** (4.6 g,

0.020 mol) in a solution containing potassium hydroxide (3.4 g, 0.065 mol), water (15 mL) and ethanol (45 mL) was heated on a steam bath overnight. The solution was then evaporated to dryness and water (40 mL) was added. The crystals that remained were removed by filtration to yield 0.9 g (20%) of *syn*-**31**, mp 184-186°C (lit. 185-185.6°C)[43]. An oil was produced when the filtrate was acidified with cold dilute sulfuric acid. The oil was extracted into ether, the ether was dried (Na_2SO_4) and then removed to yield 3.8 g of a residue that showed a quartet at δ 4.25 in the ^1H NMR ($CDCl_3$) spectrum. The residue was redissolved in basic water and dilute sulfuric acid was added until a precipitate just remained. The solution was extracted with ether and the aqueous layer worked-up as before to yield 1.6 g (32%) of diacid *anti*-**32**, mp 205-207°C (lit. 206-209°C)[43]. Failure to remove all traces of mineral acid from the ether layer prior to evaporation often resulted in the formation of the anhydride *anti*-**31** which melts at 190-193°C[43]. The ether solution containing the material that just precipitated when the original solution was partially acidified was dried and the ether was removed. The residue was recrystallized from methanol to yield 0.3 g (6%) of *anti*-**32e**, mp 114.5-115°C; IR (film) 3500-2200, 1740, 1720, 1700, 1680, 1300, 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.25 (q, 2H), 2.90-2.50 (br m, 4H), 2.25-

0.85 (br series of m, 15H); MS, m/e 278 (M^+), 194 (base).

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.17; H, 7.98.

Methyl Hydrogen 1,2,3,4,4a,5,6,7,8,8a-Decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a,8a-dicarboxylate (*anti*-32m). A mixture of anhydrides *syn* and *anti*-**31** (59.5 g, 0.256 mol) in a solution of absolute methanol (300 mL) that had been treated with sodium metal (10 g, 0.45 mol) was heated in a glass pressure bottle at 80°C for 5 h. Higher temperatures or longer reaction times were found to produce significant amounts of *syn* and *anti*-**32** (*vide infra*). The solution was then evaporated to dryness, water (200 mL) was added and the crystals that remained were removed by filtration to yield 16.0 g (26.9%) of *syn*-**31**. The filtrate was extracted with ether (1 X 100 mL), which was discarded, and acidified with 3 M sulfuric acid (60 mL). The solution was extracted with ether (3 X 100 mL) and the combined extracts were washed with water (2 X 20 mL) and dried. This was concentrated to about 80 mL and an equal volume of pentane added. The crystals that formed were then removed by filtration to yield 41.8 g (61.7%) of *anti*-**32m**, mp 116-8°C; IR (film) 3500-2200, 1710, 1682, 1265, 1245 cm^{-1}; ^1H NMR (acetone-d_6) δ 3.72 (s, 3H), 2.80-2.60 (br s, 2H), 2.60-2.40 (br s, 2H), 2.40-2.00 (br overlapping acetone), 1.95-1.00 (series of m, 10H); MS, m/e 264 (M^+), 198 (base).

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63 Found: C, 68.08; H, 7.63.

1,2,3,4,4a,5,6,7,8,8a-Decahydro-1,4:5,8-*exo,exo*-dimethanonaphthalene-4a,8a-dicarboxylic Acid (*syn*-32). Anhydride *syn*-**31** (4.6 g, 0.020 mol) in a solution of absolute methanol (100 mL) that had been treated with sodium metal (2.5 g, 0.11 mol) was heated in a metal high pressure cylinder at 150°C for two days. The cooled mixture was evaporated to dryness, water (50 mL) was added and no crystals remained. This was extracted with ether (50 mL), which was discarded, and then acidified with 3 M sulfuric acid. It was then extracted with ether (2 X 30 mL) and the combined extracts were washed with water (5 X 10 mL) and dried. The solution was then evaporated to dryness to yield 4.1 g (82%) of *syn*-**32**, mp 206-208°C which after a few weeks fell to mp 175-185°C presumably due to reformation of some anhydride *syn*-**31**; IR (Nujol) 3700-3200, 3000-2800, 2700-2100, 2000-1800, 1690, 1580, 1270 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10-6 (br, 2H), 2.75-2.25 (br overlapping DMSO), 1.80-1.00 (series of br s and m, 11H), 0.90 (s, 1H); MS, m/e 206 (M^+-CO_2), 139 (base).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.36; H, 7.53.

***Anti*-32 from *anti*-32m.** Acid-ester *anti*-**32m** (1.6 g, 6.1 mmol) in a solution of absolute methanol (40 mL) that had been treated with sodium metal (1.2 g, 0.052 mol) was heated in a metal high pressure cylinder at 150°C overnight. Work-up was similar to that for *syn*-**32** and yielded 1.3 g (85%) of *anti*-**32**, mp 205-207°C. Mixed mp with authentic *anti*-**32** gave mp 205-207°C.

Methyl Hydrogen 1,2,3,4,4a,5,6,7,8,8a-Decahydro-1,4:5,8-*exo,exo*-dimethanonaphthalene-4a,8a-dicarboxylate (*syn*-32m). Anhydride *syn*-**31** (8.0 g, 0.034 mol) in a solution of absolute methanol (50 mL) that had been treated with sodium metal (0.8 g, 0.035 mol) was heated in a metal high pressure cylinder at 150°C for 1.5 h. The cooled mixture was evaporated to dryness, water (50 mL) was added and the crystals that remained were removed by filtration to yield 6.8 g of *syn*-**31**. Work-up was similar to that for *syn*-**32** and yielded 1.2 g of a solid having a wide melting point range. This was recrystallized from ether-pentane to give 0.2 g of **32m**, mp 197-200; IR (Nujol) 3500-2300, 1720, 1635, 1305, 1260 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.83 (s, 3H), 2.80-2.25 (br overlapping DMSO), 1.70-1.02 (series of br s and m, 11H), 0.97 (s, 1H); MS, m/e 233 (M^+-CH_3O), 153 (base).

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.16; H, 7.76.

Methyl 8a-Acetoxy-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a-carboxylate (34). Lead tetraacetate (75 g, 0.17 mol) was added to a solution containing acid-ester *anti*-**32m** (42.3 g, 0.160 mol), benzene (400 mL) and acetic acid (100 mL). This solution was refluxed on a steam bath until the initial light yellow color completely vanished, usually 15 to 20 h. The solution was then washed with water (2 X 100 mL) and then with dilute sodium hydroxide until the washings remained basic. A black precipitate, PbO_2, usually developed during this procedure and was removed by gravity filtration. These basic washings were acidified with dilute sulfuric acid and extracted with ether. The ether extract was washed with water, dried and concentrated to about 20 mL and an equal volume of pentane was added. This was kept at 2°C overnight and the ether-pentane was decanted from the crystals that formed to yield 6.2 g of starting material *anti*-**32m**. The benzene solution was washed with water, dried and concentrated to about 100 mL and an equal volume of pentane was added. This was left at 2°C overnight and the benzene-pentane decanted from the crystals that formed to yield 21.0 g of **34**, mp 120-121.5°C; IR (film) 3060, 2980, 2880, 1742, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.64 (s, 3H), 3.22-3.05 (br, 1H), 2.94-2.76 (br, 1H), 2.64-2.38 (br, 2H), 2.26-1.90 (br series of s and m overlapping s at δ 2.07, 1H), δ 2.07 (s, 3H),

1.90-0.89 (br series, 12H); MS, m/e 278 (M^+), 250 (base).

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.02; H, 7.97.

A second crop gave 3.7 g of **34**, mp 120-121.5°C, for a total yield of 24.7 g (55.6% or 65.0% on the basis of recovered starting material). The remaining solution was evaporated to dryness to yield 9.2 g of a solid showing three overlapping spots on TLC (ether) and vinyl protons in the ^1H NMR.

8a-Hydroxy-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a-carboxylic Acid (35). A heterogeneous mixture containing ester-acetate **34** (10.0 g, 0.0360 mol) and 4.5 M sulfuric acid (80 mL) was refluxed with stirring by a magnetic stirrer until the oily organic layer had completely solidified, usually 10-12 h or overnight. The cooled mixture was then extracted with ether (3 X 75 mL) and the combined extracts were washed with water, dried and concentrated to about 50 mL and an equal volume of pentane was added. This was allowed to stand overnight at room temperature and the ether-pentane was then decanted from the crystals that formed to yield 6.5 g of **35**, mp 188-189°C (bubbles); IR (film) 3500-2000, 1678, 1475, 1278 cm^{-1}; ^1H NMR (acetone-d_6) δ 10-7 (br, 1H), 2.80-2.55 (s, 1H), 2.55-2.25 (m, 3H), 2.25-0.95 (br series of m overlapping acetone); MS, m/e 222 (M^+), 176 (base).

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.42; H, 8.20.

A second crop gave 1.1 g of **35**, mp 185-6°C (bubbles), for a total yield of 7.6 g (95%).

Acetic 8a-acetoxy-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a-carboxylic Anhydride (47). A solution of hydroxy-acid **35** (2.2 g, 0.010 mol) and acetic anhydride (40 mL) was refluxed for 5 h. This was concentrated to an oil that was dissolved in ether (20 mL). Pentane (30 mL) was then added. This solution was kept at 2°C overnight and the ether-pentane decanted from the crystals that formed to yield 2.5 g (81.6%) of **47**, mp 99.5-100°C; IR (cast) 3070, 2980, 2880, 1800, 1745, 1725, 1365, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.27-3.08 (br s, 1H), 2.96-2.78 (br s, 1H), 2.78-2.60 (br s, 1H), 2.60-2.42 (br s, 1H), 2.32-0.98 (br series of s and m overlapping s at δ 2.22 and δ 2.07, 12H), δ 2.22 (s, 3H), δ 2.07 (s, 3H); MS, m/e 306 (M^+), 176 (base).

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.60; H, 7.28.

8a-Acetoxy-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a-carboxylic Acid (48). Anhydride **47** (2.3 g, 7.5 mmol) in methanol (25 mL) was added to a solution containing sodium hydroxide (0.5 g, 20 mmol) in water (15 mL) and the solution was allowed to stand at room temperature for 30 m. This was concentrated to about 10 mL, water (25 mL) was added and the solution was extracted with ether (20 mL), which was

discarded. The aqueous layer was then acidified with dilute sulfuric acid and extracted with ether (2 X 40 mL). The combined extracts were washed with water, dried and concentrated to about 20 mL and an equal volume of pentane was added. This solution was left at 2°C overnight and the ether-pentane decahted from the crystals that formed to yield 1.4 g (71%) of **48**, mp 150-151°C; IR (film) 3500-2200, 1740, 1715, 1675, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.30-3.12 (br s, 1H), 3.00-2.75 (br s, 2H), 2.68-2.52 (br s, 1H), 2.17 (s, 3H), 2.10-1.10 (br series of s and m, 12H); MS, m/e 264 (M^+), 43 (base).

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63 Found: C, 68.39; H, 7.70.

34 from 48. The method used for the esterification of the carboxylic acid group of **48** was essentially that used by Alvarez and Watt[64] on a different molecule. A solution of acid **48** (0.26 g, 1.0 mmol), dimethylacetamide (8.7 g), sodium bicarbonate (0.2 g) and methyl iodide (0.30 g, 1.4 mmol) was kept at 30°C in the dark for 48 h. It was then poured into 10% aqueous sodium chloride solution (100 mL) and the crystals that formed overnight at room temperature were removed by filtration to yield 0.27 g (99%) of **34**, mp 120-122°C. Mixed mp with authentic **34** gave mp 120-122°C. The ^1H NMR ($CDCl_3$) spectrum was identical to that of authentic **34**.

4a-Chloro-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene (49). The general procedure used by Adam[47] for the formation of alkenes from β-hydroxy acids was used for this synthesis but **49** was isolated as the sole unexpected product. A solution of β-hydroxy acid **35** (2.2 g, 0.010 mol) benzenesulfonyl chloride (3.5 g, 0.020 mol) and pyridine (24 g) was kept at 55°C overnight. TLC (pentane) of this crude reaction mixture showed a single spot with an R_f value of 3.4/5.5 along with a smear with an R_f value of 1.8/5.5 due to solvents. The black mixture was poured into ice water (50 mL) and extracted with pentane (2 X 50 mL). The combined extracts were washed with 3 M H_2SO_4 until the washings remained acidic, saturated sodium bicarbonate (2 X 10 mL) and dried. TLC (pentane) at this point showed two spots with R_f values of 3.4/5.5 and 0.2/5.5. The spot with an R_f value of 3.4/5.5 was separated by column chromatography (silica gel/pentane). The pentane was evaporated to dryness and the resultant solid sublimed at 5 torr (50°C) several times to yield 0.2 g (10%) of **49**, mp 85-87°C; IR (Nujol) 3060, 1295, 930, 835, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.0-0.75 (series of overlapping s and m); MS, m/e 198 (17.4%, isotopic), 196 (55.4%, M^+), 66 (base).

Anal. Calcd. for $C_{12}H_{17}Cl$: C, 73.27; H, 8.71; Cl, 18.02. Found: C, 73.40; H, 8.80; Cl, 18.20.

Anti-1,2,3,4,5,6,7,8-Octahydro-1,4:5,8-dimethanonaphthalene (*anti*-25). Olefin *anti*-25 was made by an adaptation of the general procedure of Adam[47] for the formation of alkenes from β-hydroxy acids. A solution of β-hydroxy acid **35** (3.30 g, 0.0148 mol), triethylamine (6.6 g, 0.065 mol) and pyridine (20 g) was heated to 95°C under argon in a three-neck flask equipped with an efficient condenser and benzenesulfonyl chloride (6.0 g, 0.034 mol) was added. The solution immediately turned red and became very dark after it had been heated at this temperature for 6.5 h. Addition of benzenesulfonyl chloride to a solution containing just pyridine and triethylamine also produced this red color. The solution was then cooled and extracted with pentane (5 X 50 mL). Large amounts of a solid salt formed during this procedure and were discarded. The combined extracts were washed with water (2 X 50 mL), dilute sulfuric acid until the washings remained acidic, saturated sodium bicarbonate (2 X 10 mL) and dried. TLC (pentane) of this solution showed a large spot with an R_f value of 4.2/5.5 and a small spot with an R_f value of 2.0/5.5. The spot with R_f value 4.2/5.5 was separated by column chromatography (silica gel/pentane) and the solvent evaporated to yield 0.80 g (34%) of *anti*-25, mp 64-65°C (lit 64-65°C)[43]; MS, m/e 160 (M^+), 104 (base).

49 from *anti*-25 and Pyridinium Hydrochloride. Dry hydrogen chloride produced by the addition of 35% hydrochloric acid to concentrated sulfuric acid was bubbled through pyridine. The amount of pyridinium hydrochloride produced was not determined. A small amount of *anti*-**25** (~1 mmol) was heated in this solution (3 mL) at 70°C overnight. TLC of this solution showed only a single spot with an R_f value of 3.4/5.5 and the usual solvent smear. Work-up similar to that previously described for **49** and gave **49**, mp 85-87°C. Mixed mp with authentic **49** gave mp 85-87°C.

***Anti*-25 from 49.** Treatment of **49** (~1 mmol) with triethylamine (0.5 g, 5 mmol) in pyridine (3 mL) at 100°C for 8 h failed to produce any olefin *anti*-**25**. TLC (pentane) showed only a single spot with an R_f value of 3.4/5.5 corresponding to starting material **49**.

In an attempt to prepare hydrocarbon **50**, chlorocarbon **49** (~1 mmol) in ether (2 mL) was treated with magnesium metal (0.1 g, 4 mmol) but would not react to form a Grignard even after 20 m of continuous scratching of the magnesium metal with a glass stirring rod. The solution remained clear and TLC (pentane) showed only starting material **49**. In order to start the reaction a small amount of 1,2-dibromobutane was added. When the bubbling had subsided, TLC (pentane) showed two spots with R_f values corresponding to **49** and *anti*-**25**. The ether solution was

washed with dilute hydrochloric acid, dried and concentrated to an oil. This oil was shown to decolorize a dilute solution of bromine in pentane indicating that olefin had been produced. In a second run, 1,2-dibromobutane (0.1 g, 5 mmol) was added to the same solution and only a single spot with an R_f value of 4.2/5.5 was observed by TLC (pentane). This was isolated by the procedure previously described for *anti*-**25**, and gave *anti*-**25**, mp 64-65°C. Mixed mp with authentic *anti*-**25** gave mp 64-65°C.

8a-Bromo-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a-hydroperoxide (51a). 1,3-Dibromo-5,5-dimethylhydantoin (0.20 g, 0.69 mmol), **3b**, was added over a period of 30 m to a solution at 0°C containing ether (5 mL), 98% hydrogen peroxide (0.2 mL, 6 mmol) and olefin *anti*-**25** (0.20 g, 1.3 mmol). Ether (25 mL) was added and the solution was then washed with water (5 X 10 mL) and dried. TLC (toluene) showed two spots with R_f values of 2.8/5.5 and 5.0/5.5. The slower moving spot gave off bright light when the TLC plate was heated on a hot plate. This material was isolated by column chromatography (silica gel, pentane-ether). It showed a small amount of broad absorption at 3600-3300 cm^{-1} in the IR (Nujol) and reacted slowly with silver nitrate in methanol to form a grey precipitate. It was stable indefinitely at room temperature in benzene or

ether solutions or on dry TLC plates, but when concentrated to an oil and left at room temperature overnight, the initial oil solidified and no longer gave off light when heated.

8a-Iodo-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-*exo,endo*-dimethanonaphthalene-4a-hydroperoxide (51b), 3,4:3,4-*exo,endo*-Di (1,3-cyclopropano)-1,2-dioxetane (24) and *anti*-2,5:7,10-Dimethano-1,6-cyclodecanedione (*trans*-52). 1,3-Diiodo-5,5-dimethylhydantoin (0.060 g, 0.16 mmol), **3c**, was added over a period of 10 m to a solution at -20°C containing ether (5 mL), 98% hydrogen peroxide (0.1 mL, 3 mmol) and olefin *anti*-**25** (0.050 g, 0.31 mol). Ether (25 mL) was added and the solution was then washed with water (3 X 10 mL), 5% sodium thiosulfate (2 X 10 mL), saturated sodium chloride (1 X 10 mL) and dried. TLC (toluene) of this solution showed two spots with R_f values of 2.2/5.8 and 5.1/5.8. The slower moving spot was very much smaller than the faster and gave off a bright light when the TLC plate was heated on a hot plate. The solvent was changed to dichloromethane without separating the two spots. Small portions of this solution containing **DBA** gave off light at room temperature when silver acetate was added and were used for the experiments described in the Discussion and Results section that showed that dioxetane **24** was too unstable to be isolated. Some of this solution treated overnight with excess silver

acetate in the absence of **DBA** was evaporated to dryness and the silver salts were extracted with ether. The solid obtained when the ether was evaporated to dryness was sublimed twice to yield a very small amount (10 μg) of impure diketone *trans*-**52** mp 155-185°C; IR (Nujol) 1665, 1275, 855 cm^{-1}; MS, m/e 192 (13.6%, M^+), 151 (99.7%, 55 (base); Dinitrophenylhydrazone, mp 310°C (exploded to liquid).

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